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VOLUME 30, No. 9

AMERICAN

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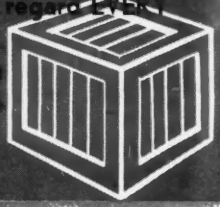

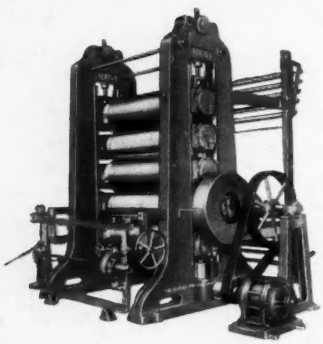

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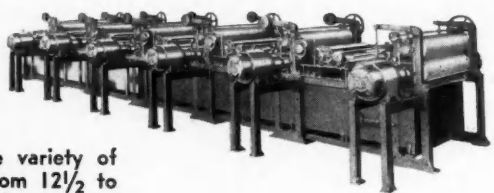

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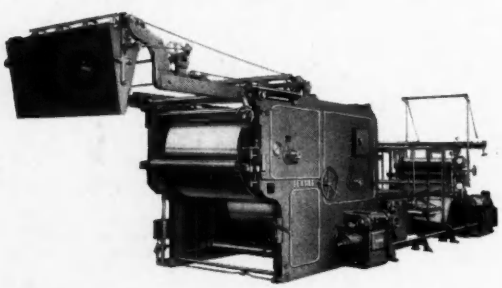

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APRIL 28, 1941

VOLUME 30 NUMBER 9

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AMERICAN
DYESTUFF REPORTER

VOLUME 30 APRIL 28, 1941 NUMBER 9

Investigation of

ALCOHOL EXTRACTS from FINE WOOL

H. C. HALLER*

IN many laboratories the purpose of making extractions on scoured wools is two-fold. First, an extraction to remove grease and oil is made with a solvent such as carbon tetrachloride ether, or similar solvents as a check on the efficiency of the scouring operation. The sample thus freed of oils and grease is dried and then extracted with ethyl alcohol presumably to remove any residual oil or grease not removed by the first extraction and any soap retained by the wool from the scouring operation.

While the first part may be done in either the Soxhlet apparatus, or by one of the rapid methods, the alcohol, or second extraction, is done only in the Soxhlet. This requires the use of boiling alcohol and usually involves about 1½ hours of time. Since the rate at which the alcohol distills over is much slower than the lower boiling point solvents, the extra time is necessary.

There are two lines of thought concerning the substance removed by the alcohol. One is that the solvents used for removing the oil and grease fails to take out an oil which some believe to be in the center of the fiber. The other is that some soap is left from the scouring operation. This soap is supposed not to be dissolved by the solvents used in the first extraction. In either case, alcohol is employed to take out the remaining substance.

So strong is the soap theory that even today there are many plants which set certain specifications as to the alcohol extract from their scoured wools.

In some instances, too, we read about the purification of wool fiber by alcoholic extraction. This is done to give a fiber free of impurities and suitable for the purpose of research.

The author has felt that although considerable work has been published along these lines, that some additional work might be helpful. Expressed in every day language, it should be quite convincing for the layman.

Ryberg[1] has shown that the alcohol extract, even when made on solvent extracted wool, is 1 per cent or better, and in the case of soap cleansed wool less than one-half the alcohol extract is actually soap. Skinkle[2] tells that if carbon tetrachloride is used for extraction purposes it is capable of removing some soap through solvent action, therefore adding error to error in the alcohol extract. Von Bergen[3] supports this thought, too.

For this work a Wyoming grease wool was selected.

First, the wool was cleansed with carbon tetrachloride to remove the bulk of dirt and grease. When dry it was then scoured with Gardinol WA in warm water, finally rinsing thoroughly and drying.

Following in the order given below extractions were made. After each extraction a small sample of the wool was taken for pH determination and miscroscopic examination.

(1) Carbon tetrachloride
(2) Carbon tetrachloride
(3) Alcohol
(4) Alcohol
(5) Alcohol
(6) Alcohol

No soap was used in cleaning this wool and the second extraction with carbon tetrachloride was to make sure that practically all the grease and oil was removed. The following results were obtained:

Extraction	*Amount of Extract* %	*Ph.*
1. Carbon Tetrachloride, 1 hr.	1.43	7.5
2. Carbon Tetrachloride, 1 hr.	.11	7.5
3. Alcohol 1 hr.	1.95	6.5-7.0
4. Alcohol 1 hr.	.19	6.5-7.0
5. Alcohol 1 hr.	.50	6.5
6. Alcohol 1 hr.	.85	5.5

The successive alcohol extractions were made to determine if there was a point at which no additional extract could be obtained. Probably as long as extractions are made on the same sample, some substance will be removed.

We then examined the extracts for their general properties and reactions. The extracts from the carbon tetrachloride acted like a true grease or oil. It charred, was insoluble in water, soluble in ether and alcohol.

*Chemist, Continental Mills, Philadelphia, Pa.

	Solubilities					*Protein Tests*		
Sample	*Appearance*	*Water—pH*	*Alcohol*	*Carbon Tet.*	*Caustic*	*Millon's test*	*Biuret*	*Organic Matter*
1.	Yellow, oily somewhat crystalline	Partly soluble, cloudy—gives stable lather when shaken pH—5.0	Partly soluble, Lt. colored Cloudy sol.	Sl. sol. breaks up and ppts.	Partly sol. Cloudy	Neg.	Pos.	100%
2.	Brownish, hard paste rather dry	Partly soluble, Sl. Cloudy Lather not stable pH—6.0	Partly soluble, Lt. colored Clear sol.	Sl. Sol. breaks up and ppts.	Partly sol. Clear	Neg.	Pos.	100%
3.	Yellow, oily somewhat crystalline	Partly soluble, Sl. Cloudy No Lather pH—4.5-5.0	Partly soluble, Lt. Brown fairly clear Sol.	Insoluble cold or hot	Partly sol. Cloudy	Neg.	Pos.	100%
4.	Yellow, oily partly crystal-line	Partly soluble cloudy No lather pH—4.5	Partly soluble, Partly ppt. Brownish Sol.	Slightly sol.	Partly sol. Clear	Neg.	Pos.	100%

In each of the alcohol extracts there was a difference in appearance, color or consistency. Solubilities in various reagents, pH of water solutions, tests for protein, both with Millon's reagent and the biuret reaction, were recorded. This was done on the alcohol extracts only, for we felt satisfied that the carbon tetrachloride took out oil and grease.

A test for amount of organic matter was made. When we took a known weight of each extract and evaporated it with concentrated sulphuric acid there was no residue at all. Above is a chart of the results of the tests.

Tying in the facts, we find that the extracts first taken up with distilled water were soluble and showed acidic conditions. The solutions were cloudy and filtering failed to clear them. This suggests a part being in colloidal suspension.

A standard wool solution made of wool dissolved in caustic was used as control in a check for protein. An excellent test was obtained with the biuret reaction on the standard and each extract.

The remainders of the water solutions when again dried, changed in properties. What was all alcohol soluble becomes only partly soluble after this drying.

The microscopic appearance of the wool samples taken after each extraction are very interesting and significant.

	Microscopic Appearance	*Handle*
(1) Clean Fiber	Very good condition. Scales very definite and showed good formation. Scales smooth	Soft
(2) 1st Carbon Tet.	Similar condition but somewhat cleaner	Soft
(3) 2nd Carbon Tet.	Similar	Soft
(4) 1st Alcohol	Scales have appearance of having been leeched. The surfaces faces are pitted.	Harsh
(5) 2nd Alcohol	Pitting more prominent. Scales are less distinct.	More Harsh
(6) 3rd Alcohol	Additional damage apparent. Greater frequency in pitting and scales are even more blunt.	Increased Harshness
(7) 4th Alcohol	Worst condition of all. Pitting much more pronounced. Scales hardly protrude because of bluntness	About the same

Remembering that the extracts showed a substantial content of protein, this agrees with the fiber loss and damage as seen under the microscope.

SUMMARY

With the evidence from this experiment we know that alcohol extracts from wool consist of proteins or in part or portion of the fiber itself. The tests for protein in the extracts and in the standard wool solution gave positive indication. The solubility of the extracts in water discards the oil theory and the acidic conditions disprove the soap angle.

Evidently alcohol extractions on wool are a valueless guide to the completeness of a scouring job.

The "purifying" of wool fibers before being used for research work may alter the fiber sufficiently to give misleading final results.

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Relative Affinities of the Anions of STRONG ACIDS FOR WOOL PROTEIN*

JACINTO STEINHARDT, CHARLES H. FUGITT, and MILTON HARRIS**

ABSTRACT

The fastness of wool dyes to washing varies widely not only among different classes of dyes but even among members of a given class. These variations are manifestations of the differences in affinities of the dyestuffs for the fibers. A possible basis for understanding such differences in affinities was described in two earlier papers in which it was shown that wool immersed in hydrochloric acid solutions combines not only with hydrogen ions but with chloride ions as well. As a consequence of this, it appeared that the affinities for wool of the anions of different acids might vary considerably and that therefore the positions of the titration curves with respect to the pH axis might vary by correspondingly large amounts, according to the acid used. The determination of the titration curve of wool with a given acid could then be used to measure the affinity of the anion of the acid for the fiber.

Measurements have therefore been made by Research Associates of the Textile Foundation at the National Bureau of Standards of the combination of wool with nineteen different acids, including, in addition to some of the common mineral acids, several of the simpler aromatic sulfonic, carboxylic, and phenolic acids and a soluble mono-azo acid dye. Wide differences were found between the positions of the resulting nineteen titration curves. A generalized form of the equations previously developed to account for the effect of the concentration of chloride ion on the amounts of hydrochloric acid combined was utilized to calculate the affinity for wool of each of seventeen anions involved. Predictions, based on the equations, as to the effects of variations of anion concentrations and of temperature were tested and confirmed.

Measurements of the combination of a number of the same acids with a soluble protein, crystalline egg albumin, were also made. Since qualitatively similar differences in the corresponding titration curves were found with both proteins, it is concluded that the property of combining with anions is not restricted to insoluble proteins, such as wool, but is an inherent property of proteins in general. The affinity of the anions appears to increase with their dimensions, and is higher in aromatic than in aliphatic ions of the same size. These relationships are used as the basis of a consideration of the nature of the forces involved in the binding by proteins of anions, including the anions of acid dyes.

I. INTRODUCTION

IT is well recognized that the fastness of wool dyes to washing, and their related properties of exhausting onto wool or other protein fibers from a dyebath, vary widely not only among different classes of dyes, but also among the members of a given class. These variations are frequently regarded as manifestations of differences in affinity of the various dyestuffs for the fibers. The existence of similar differences in the affinities of ions for proteins in general is suggested by the frequently reported and repeatedly investigated instances of specific differences in the effects of various ions on protein behavior.

A possible basis for understanding such specific effects in terms of the participation of the anions of acids and the cations of bases in the combination of wool protein with acid and base has already been described in two earlier communications[36, 38]. Evidence was presented in support of the view that the combination of wool with hydrochloric acid may be resolved into two partial reactions, one with hydrogen ions and one with chloride ions, and that each reaction is governed by its own equilibrium constant. On the basis of this assumption it proved possible to account for the large effects produced by varying the concentration of potassium chloride on the combination of wool with hydrochloric acid. Among other consequences of this view was a strong possibility that the specific affinities for wool of the anions of different acids might vary considerably, and that therefore the positions of the titration curves of this and other proteins with respect to the pH axis might vary by correspondingly large amounts according to the acid used. The existence of such a variation would constitute critical evidence in support of the hypothesis of anion association, since alternative analyses of the effect of salt, based upon the

*Part of the material in the present paper was presented at the meeting of the American Society of Biological Chemists at New Orleans, Louisiana, in March, 1940[37].

**Research Associates at the National Bureau of Standards, representing the Textile Foundation.

Donnan membrane-equilibrium equations[36], offer no obvious basis for the prediction of such an effect.

The present paper describes measurements of the combination of wool with nineteen different acids, ranging in complexity from some of the mineral acids most commonly used in the laboratory through the simpler aromatic, sulfonic, carboxylic, and phenolic acids to a soluble monoazo acid dye. The acids employed were selected from among those readily available with the purpose in view of obtaining data which could be simply calculated, and interpreted in terms of molecular size, chemical structure, and the effects of specific substituents. For this reason most of the results reported in the present paper deal with acids which are mono-basic and virtually totally dissociated in water. A limited number of weak acids which are analogues of some of the strong acids used (e.g., benzoic acid is analogous with benzenesulfonic acid in the sense used here) have been included for the specific purpose of examining the effects of this analogy. An effort has also been made to include organic acids with all of the more common dissociating groups. Since strong acids containing carboxylic or phenolic radicals as dissociating groups can be obtained only by loading with substituents such as halogens or nitro groups, other related acids have been included in order to make possible an independent appraisal of the effect of various substituent groups, and of more strictly physical factors such as the size and shape of the anion produced.

In order to determine whether differences in affinity between the ions of different acids are restricted to wool, or to the insoluble class of proteins for which the theory of anion-association was specifically proposed[36], measurements have also been made of the combination of a number of the same acids with a well-characterized *soluble* protein, crystalline egg albumin. Demonstration that the hypothesis of anion association is applicable to both would have an obvious bearing on the interpretation of the titration curves of both classes of proteins and of the wide range of phenomena which depends on the combination of protein with acid or base.

II. EXPERIMENTAL PROCEDURE

Details of the purification of the wool and of the method used in measuring pH values and the amounts of acid combined have already been described[36, 38].

Additional details which concern the materials used in the present investigation, and modifications of the procedures previously described as well as detailed tables of the experimental data, are given in a more detailed version of this paper published in the Journal of Research of the National Bureau of Standards.

III. RESULTS AND DISCUSSION

1. Results Obtained in the Absence of Salts

The results obtained with 16 different strong acids in the absence of salt at 0° C. are represented in Fig. 1. In drawing the curves an effort has been made to represent the measurements fairly with smooth curves rather than to preserve the appearance of homogeneity of the data. The resulting tendency of certain neighboring curves to

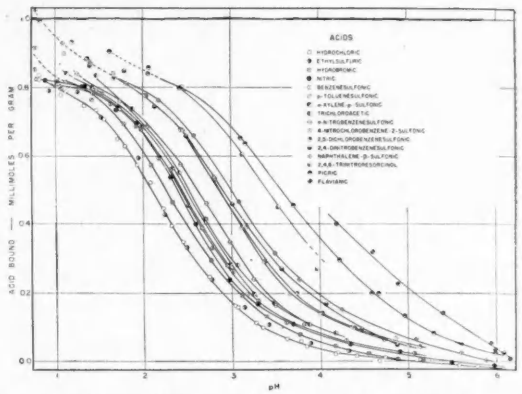

Figure 1—The combination of wool protein with sixteen different strong acids as a function of pH at 0° C. The measurements with flavianic acid are represented in milliequivalents instead of millimoles. Points representing the combination of less than 0.14 millimole per g. of three acids (*p*-toluenesulfonic, *o*-xylene-*p*-sulfonic, and *o*-nitrobenzenesulfonic) would fall at lower pH values than are required for congruence with the curves for the other acids, and have been omitted to avoid confusing the figure. Data for the two dibasic acids, flavianic and trinitroresorcinol, are only partially represented, as explained elsewhere.

cross or converge is usually within the range of effects which may be ascribed to experimental error.

The most noticeable feature of the data in Fig. 1 is the wide range of positions with respect to the pH coordinates which the titration curves occupy. It is also apparent that except for minor deviations the curves form a coherent family, near neighbors following a fairly parallel course. The change in the slopes of the lower portions of the curves, from the more sharply inflected curve for hydrochloric and ethylsulfuric acids at one end of the pH range to the less sharply inflected curves for picric and flavianic acids at the other end, tends to be gradual and progressive. The appearance of the curves as a group is entirely consistent with the view that they all describe analogous phenomena.

It is a familiar fact that the position on a pH grid of the titration curves of the common weak bases is determined by their own dissociation constants and not by the dissociation constant or by other chemical properties of the acid employed in the titration. Sets of titration curves obtained with any number of weak or strong acids would be expected to be practically superimposed on one another. Exceptions arise, as in the work of Cannan and Kibrick[7] and of Greenwald[16, 17] with carboxylic acids and phosphates, when the compound formed by the reaction of the base with certain acids is not typically salt-like and does not exist in solution predominantly in the dissociated form. These exceptions find their counterparts, in the case of ampholytes, in the formation of only partially dissociated stoichiometric complexes between the anions of the acids and the ampholyte which has combined with hydrogen ions. When these are formed, the positions of the titration curves and to a lesser extent their shapes, will differ according to the extent to which the anion is dissociated[36].

(Concluded on page 246)

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Meeting, Philadelphia Section, Penn A.C., Philadelphia, Pa., May 2, 1941.

Meeting, Southeastern Section, Ralston Hotel, Columbus, Ga., May 3, 1941. Speaker: Hugh Comer, Avondale Mills.

Meeting, South Central Section, Farragut Hotel, Knoxville, Tenn., May 17, 1941.

Meeting, New York Section, Swiss Chalet, Rochelle Park, N. J., May 23, 1941. Speaker: J. O. Amstuz, Behr Manning Corp., Troy, N. Y., "Electrocoating Fabrics."

Meeting, Rhode Island Section, May 30, 1941.

Outing, Mid-West Section, Lake Lawn, Delavan, Wis., June 14, 1941.

Outing, New York Section, North Jersey Country Club, Paterson, N. J., June 20, 1941.

Outing, Philadelphia Section, Whitemarsh Valley Country Club, June 20, 1941.

Outing, Rhode Island Section, Norwich Inn, Norwich, Conn., June 20, 1941.

Annual Meeting and Convention, Carolina Hotel, Pinehurst, N. C., Oct. 31, Nov. 1, 1941.

Technical Evaluation of

TEXTILE FINISHING TREATMENTS

VI. The Effect of Relative Humidity on Flexibility; Test Methods for the Drapeometer

LELIA J. WINN* and EDWARD R. SCHWARZ, F.T.I.**

Abstract

The relative humidity has been shown to have a definite effect on fabric stiffness. The stiffness increases as the relative humidity is lowered. Methods of handling the Drapeometer are given.

IN addition to any finishing treatment which may be given to fabric, the testing of stiffness or of draping quality may be influenced by external conditions. Among these, time and humidity are important. In this brief and final study of the present series, tests on a limited number of fabrics are outlined. Four of the eight standard samples previously tested—the Rayon material, the Tag Cloth, the Mulle Sheer and the Glazed Chintz—were tested on the Drapeometer to find the effect of relative humidity on the stiffness value. Five specimens were cut warpwise and five fillingwise from each material at random and were tested face out. The chord length was measured at 0, 2, 4, 6, 9, 12, 15, 18, 21, and 24 centimeters down the specimen, both by means of a telescope mounted on a horizontal cathetometer and by means of the Drapeometer and the Drapeogram. The cathetometer test took 10 minutes to complete, then a Drapeogram was made in the next 10 minutes, after which the first readings were checked by the cathetometer both to show any change in the specimen over the elapsed time and since the action of the automatic humidity control is intermittent. The samples were tested first at a high humidity, then at a low humidity, and then at approximately standard conditions. The average of the five readings tested in the same direction of the fabric and the combined average of the warp and filling directions were used at each chord length to make graphs of chord length versus height for both directions of each sample and for the sample as a whole. The value at 18 centimeters was used for comparison within and between the samples.

It was found that the shape of a specimen usually changed very little between 10 and 20 minutes of hanging on the drape disc. The fabric often curved slightly more, but in some cases it tended to straighten out. The average chord length at 18 centimeters of the Rayon material after it had hung for 20 minutes was 99.7 per cent and the average warpwise chord length of the Mulle Sheer was 99.3 per cent of the average chord length at 10 minutes. In every other instance the average chord length was wider after hanging for the longer period of time. The largest change was seen in the Tag Cloth filling which averaged 101.2 per cent of the chord length at 10 minutes.

When the readings were checked by means of a cathetometer held in a horizontal position, the telescope was mounted on a pivot so that it swung in a vertical arc. The Drapeometer measuring rod, without the pointer, was placed close to the edge of the specimen at the level which was to be measured. The edge of a pliable specimen is so nearly vertical that the rod seldom had to be moved during a test. The telescope was swung until the cross hair was at the correct level as read from the rod. Then the telescope was moved horizontally by means of the cathetometer support and readings were taken when the cross hair was on each outside edge of the specimen. The difference in these two readings was the chord length in centimeters as measured at right angles to the base. The cathetometer was adjusted so that it was parallel to the edge of the Drapeometer behind the drape disc, and leveled so that the telescope cross hairs read at the same height on either side of the drape disc.

The values obtained by the cathetometer and the Drapeogram checked very well. The Drapeogram values averaged .10 centimeter less than the cathetometer values after an allowance had been made for any change in the fabric after it had hung for the longer period of time. When the Drapeometer pointer was checked against a rule the instrument showed .06 less than the distance on the rule. Since the Drapeogram distance is two-thirds the actual value, .06 is multiplied by 3/2 to give a difference of .09 centimeter due to the adjustment of the instrument. Thus the Drapeogram, when it is correctly adjusted, is as accurate as a cathetometer which reads to 0.1 centimeter.

The relative humidity in the room where the tests were made varied from a high to a low point over approximately 10-minute periods. The average value would be about midway between the two extremes which are reached *momentarily* as the vapor spray is turned on or off. The extreme values for the high relative humidity range were 62 per cent and 94 per cent. The medium relative humidity range varied from 57 per cent to 71 per cent for the

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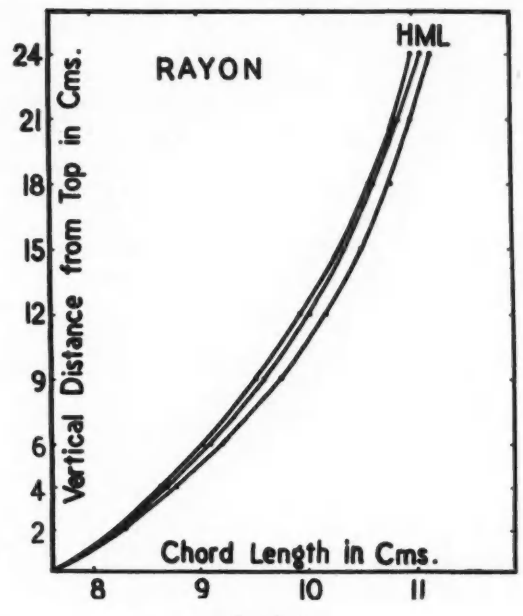
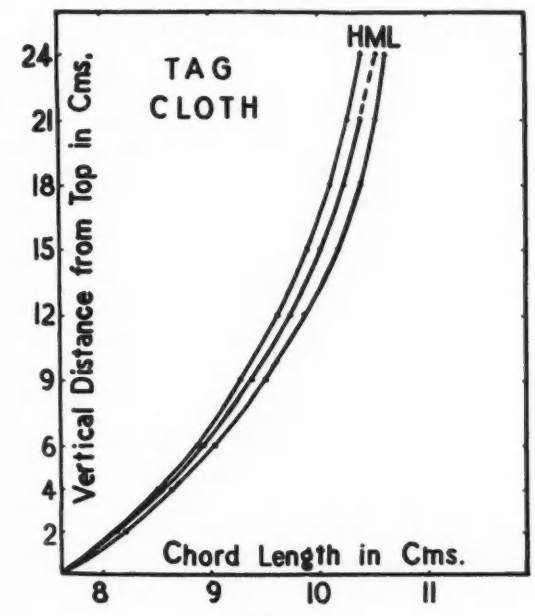
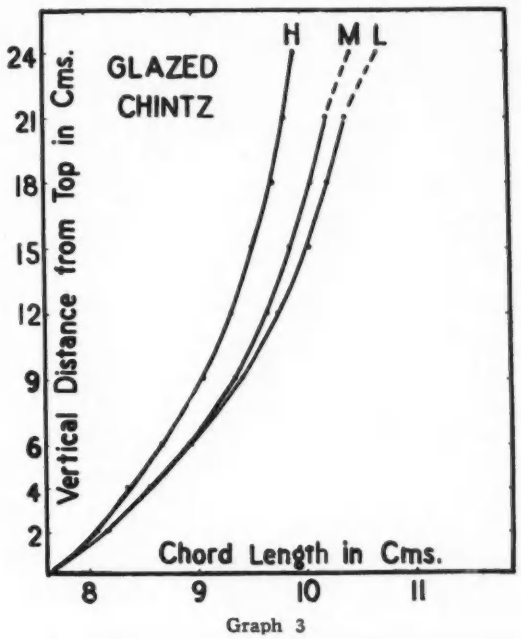


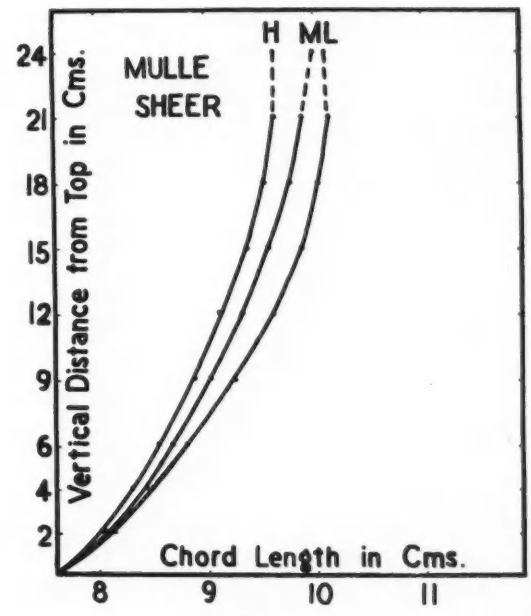
Graph 1



Graph 2



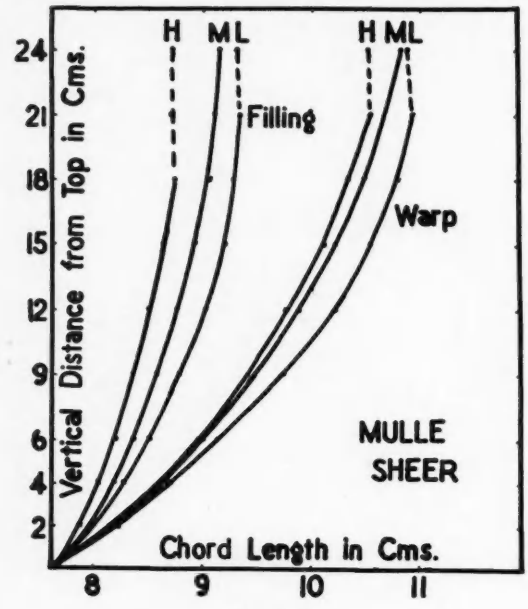
Graph 3



Graph 4

Rayon material, 55 per cent to 79 per cent for the Tag Cloth, 52 per cent to 77 per cent for the Glazed Chintz, and 51 per cent to 83 per cent for the Mulle Sheer. The spray system was shut off for the low relative humidity range and the tests were made under ordinary room conditions. Thus the relative humidity varied only from 25 per cent to 30 per cent except for the Tag Cloth filling where it rose from 33 per cent to 36 per cent. Such variations in relative humidity are similarly found in industrial conditions. These three widely different relative humidity conditions were necessarily chosen because of the fluctuation during a test. However, significant variations between the stiffness values found at these ranges show the possibilities of tests under more accurately controlled conditions. The stiffness of the four materials tested increased as the relative humidity was lowered.

The tests made in the warp direction show the most change in stiffness values and therefore the largest number of significantly different stiffness values, even though in the Rayon material it is the more pliable direction tested.



Graph 5

The average chord lengths at 18 centimeters and the standard deviations within the specimens tested in the same direction are shown in Table I for each sample at each relative humidity range.

TABLE I

		Warp Tested		*Filling Tested*	
	Relative Humidity Range	*Average Chord Length*	*Standard Deviation*	*Average Chord Length*	*Standard Deviation*
Rayon					
	High	10.40	.068	10.75	.101
	Medium	10.56	.082	10.69	.071
	Low	10.78	.057	10.79	.085
Tag Cloth					
	High	10.95	.252	9.28	.194
	Medium	11.27	.262	9.23	.090
	Low	11.42	.194	9.36	.298
Glazed Chintz					
	High	10.68	.293	8.73	.154
	Medium	11.11	.149	9.03	.169
	Low	11.21	.238	9.23	.295
Mulle Sheer					
	High	10.34	.166	8.73	.318
	Medium	10.49	.081	9.07	.149
	Low	10.80	.172	9.28	.159

The warp direction of the Rayon material showed a significant difference between the stiffness values measured at each humidity range, high, middle, and low. The stiffness values for the filling direction changed so little that no significant difference was discernible. The Glazed Chintz showed significant differences in both directions between the tests made at the high and the middle humidity ranges, but no such difference was found between the stiffness as found at the middle and low humidity ranges. The Mulle Sheer showed a significant difference in stiffness between the stiffness at the middle and low humidity ranges. The Tag Cloth tests showed a significant difference only in the warp direction tests between the high and low humidity ranges.

The stiffness ranking order of the four materials did not change during the tests. At each humidity the Rayon material was the stiffest, the Tag Cloth second, the Glazed Chintz third, and the Mulle Sheer the most pliable. The graphs drawn of chord length versus height show the average chord length at each level of each material at each humidity range. The stiffness variation of a group of five specimens was quite random, except in the case of an exceptionally stiff or soft specimen. A check of the specimen number against its position in the sample showed that specimens adjacent in the material had closer stiffness values than those further apart.

The amount, or per cent, of change in the stiffness value of a sample from the high to the low relative humidity range as compared to the value at the low relative humidity (which is ordinary room condition) was small although it could be measured. The Rayon material changed the least while the Glazed Chintz and Mulle Sheer showed the most change. The per cent changes in stiffness values are given below in Table II. Since the filling stiffness values at the middle relative humidity range of the Rayon and Tag Cloth materials are lower than the values at the high relative range, though not significantly so, the per cent change in these two cases is greater between the middle and low ranges, .9 per cent and 1.4 per cent respectively, than between the high and low ranges. It is noted that the larger difference found in the Mulle Sheer was not significant because the standard deviation within the material was also large.

TABLE II

% Difference Between Stiffness Values at the High and Low Relative Humidity Ranges (In Terms of the Low R.H. Range)

	Filling	*Warp*
Rayon Material	.4	3.5
Tag Cloth	.9	4.1
Mulle Sheer	6.0	4.3
Glazed Chintz	5.4	4.7

Viscose Rayon has a higher moisture regain with 11 per cent than the cotton fabrics with 6.5 per cent. Therefore the Rayon fibers would tend to swell more with an increase in humidity than would the cotton fibers. Thus, although a higher humidity would lubricate the fibers so that they would be more flexible, the swelling would cause friction which would tend to neutralize this effect. The viscose Rayon material showed the least change of the four materials. A hard finished, dense material would show the effect of the swelling to a greater degree, and the dense Tag Cloth changed less than the open Mulle Sheer and Glazed Chintz.

TEST METHODS FOR THE DRAPEOMETER

Details of the test methods for the Drapeometer have been requested from various sources and are therefore included in this final paper.

The drape disc is adjusted for height so as to bring the pointer level with the bottom half-inch edge of the disc when the scale marker reads zero centimeters (Figure 1). A separate piece of paper (5″ x 3″ is large enough)

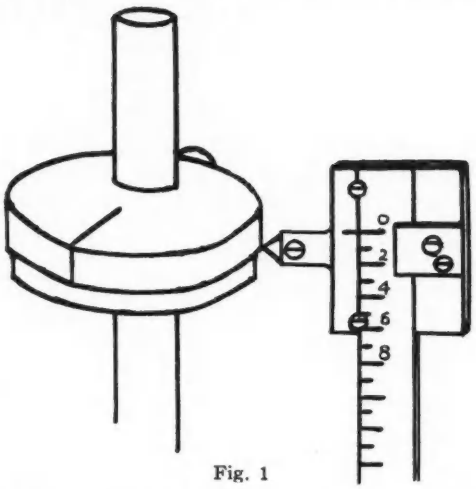


Fig. 1

may be used for each test, or a group of tests may be put on a large sheet. The base plate should be marked to indicate the correct placement of the paper. Scotch Tape will hold it in place. A small piece of carbon paper is placed face down over the paper during the test. (See also Figure 4.)

The specimen is cut from the sample with the aid of a razor blade and a metal template 4.7″ x 10″. The shorter edges should lie in the direction to be tested and follow the yarns as closely as possible (Figure 2). A soft pencil

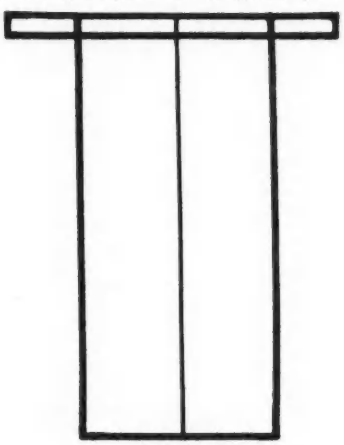


Fig. 2

line is then drawn down the center of the specimen. When the material is under some tension, as in the case of a seersucker, pieces a little larger than the specimen size should be cut and allowed to contract before they are cut to size.

An eight-inch length of half-inch width cellulose tape is attached to the specimen while it lies on a flat surface. Since the tape does not stretch, the specimen is held under an even and no greater tension when mounted on the disc. The top edge of the tape should exactly meet the top edge of the specimen and equal lengths of the tape project at each side.

The specimen is mounted on the drape disc so that their center points are coincident and the tape fits along the half-inch edge. The specimen must be correctly mounted or the test will be erratic. The top edges of the disc, specimen and tape should be level. The center line of the specimen is checked for verticality by sliding the pointer down the rod as it is held at the center position or by holding the rod in front of the line if the cloth does not slant in too far. If the specimen has been correctly cut and mounted the center line should not lean to either side. If the tape seems to sag it may be checked by holding the pointer at zero where it should just meet the bottom edge of the tape. If the tape is held at the ends, the specimen placed in position against the disc from the front, and the tape ends attached, the specimen will be found to be correctly mounted.

A Drapeogram shows the specimen's contour from the top free edge (at the bottom edge of the tape), which is the zero contour line, to its bottom edge. (Figure 3).

Fig. 3a—Normal Drapeograph. Note symmetry.

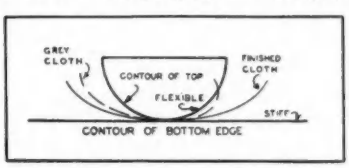


Fig. 3b—Diagram showing lack of symmetry for "grey cloth," as compared with "finished cloth."

The contour lines are drawn at successive 6 centimeter levels (or other convenient levels) down its length. At each level the pointer is first brought to one side edge of the specimen and the metal point or marker is tapped so as to make a point on the paper beneath. Then the pointer is moved about 1 centimeter in from the edge and the marker is again depressed. In this manner a line of points is made to show the contour. The center point is made at the center line of the specimen. It has been found easiest to guide the rod with the right hand at its base and to tap the marker with the left (Figure 4). If the lighting is overhead, the pointer and its shadow on the specimen just meet as the pointer touches the specimen. A different color of carbon paper is used at each level. The points are connected when the test is complete using colored pencils and a French curve.

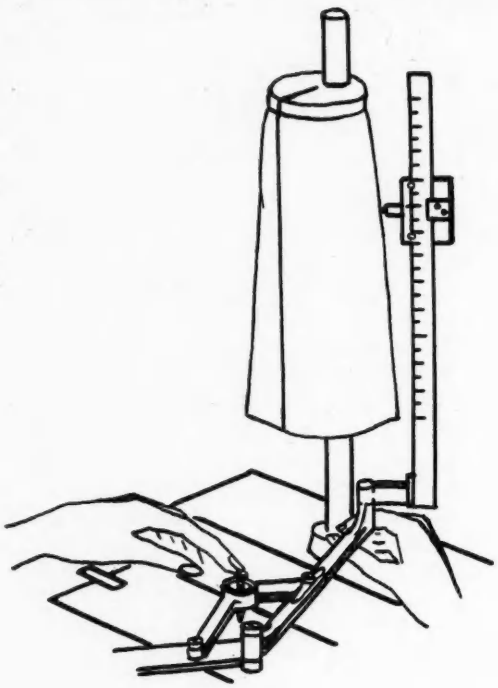


Fig. 4

The chord length is measured at a predetermined level and is read to .01 centimeter. It may be given as read from the Drapeogram or as this value times 3/2 which is the actual width of the specimen at that height. The correct level is determined by the stiffness range of the samples under test. It has been found by first plotting the readings of the chord lengths against the levels at which they were taken for each sample. The chord lengths are measured at closer intervals where the specimen flares quickly than where it is comparatively vertical. Examination of the graph thus formed will show where the range of the chord length values is greatest and most even. A level below 21 centimeters, or even less, often shows irregularities since the specimens may curl at the bottom edge. A level above 9 centimeters gives less range because the chord lengths are only partially flared from the zero line at 3 inches width. These facts are demonstrated in Graph 5 which gives the Warp and Filling curves of the Mulle Sheer. Chord lengths at several heights may then be treated statistically by means of the Analysis of Variance and the t-test (see Part V, page 690) to find the best level. Once the correct level is known for a certain type or group of samples, the chord length as measured at this level is sufficient for routine testing. It has been found that 7 inches, or 18 centimeters, is best in the case of the Tag Cloth with chord lengths from 9.86 to 10.77 centimeters, and for White Cotton Sheeting with chord lengths from 11.02 to 11.54 centimeters. Since ten minutes are allowed for a test (to allow the specimen to come to equilibrium), the specimen is allowed to hang for that period of time before the chord length is measured at the single level.

The specimens may be tested both face in and face out. The average of these two readings is the Drapeometer stiffness value for the specimen. The type of test determines whether the stiffness of the sample as a whole is desired, or whether the stiffness of one side would better suit the purpose. A specimen tests the direction of the sample which is parallel with the shorter edge.

It should be emphasized that the Drapeometer does not measure stiffness as do the other methods now in use. Rather it indicates how stiffness in conjunction with other factors affects the draping quality of the material, an important quality in many fabric uses. Factors of the composite quality may be separated out either by comparing the results obtained on the same material with different types of tests or by testing the effect of different treatments on a given fabric. Comparative tests on the first set of materials and on the eight standard fabrics used the first method. Tests on the Tag Cloth samples used the latter method and the conversion factors discussed in both Parts IV and V are similar in treatment.

The conversion factors have been fully discussed in previous articles. The possibility of choosing a level at which to measure the chord length so that the weight of the specimen is taken into account, thus giving a ranking order more similar to G, Flexural Rigidity, of the Hanging Heart Loop was discussed in Part II. The formula was $H_c = L - \frac{W_m}{W_c}(L\text{-}H_m)$. Since the weight acting on a reading at a given level is the weight below that level, the length L of 9.5 inches minus a convenient height (H_m) at which to measure a specimen times the weight (W_m) of that portion of the specimen may be compared to 9.5 minus the corrected height (H_c) at which a second specimen should be measured times the weight (W_c) of the second specimen. Such a weight correction has been found to show significant agreement in ranking order with G in the case of the Tag Cloth and the light standard samples. However, a height determined by the density of the specimen showed better agreement than the weight correction in the case of the first ten samples tested and when comparing all the samples tested as a group. In this method of height determination, since the density shows an inverse relationship to the stiffness value as measured by the Drapeometer, the chord length of a specimen of low density is read at a higher level than the chord length of a specimen of high density.

Except for the purposes of isolating such factors, the conversions from one method to another are not of immediate practical interest. The factors do not change the stiffness values when they are equally present in all the samples tested. In most cases the materials under test

(Concluded on page P238)

pH AND DETERGENCY*

DR. MALCOLM DOLE**

THERE are several reasons for studying the effect of pH on detergency. First, the washing water should not be too alkaline, otherwise the fabrics will be impaired. Second, washing waters should not be too acid, or acid soaps will precipitate. We should have the proper pH so that the surface tension will be a minimum, the interfacial tension a minimum, the contact angle a minimum, and the solid-suspending power and the detergent action a maximum. Finally, we should have some reserve alkalinity in the bath to neutralize the acids in soiled clothes, to saponify the fatty acids that may be in the dirt.

So, I think it is important for us to spend some time tonight in looking into the fundamental principles underlying pH and the influence of pH on detergent action.

What do we mean by pH? First of all, I want to remind you that water itself ionizes, due to self-impact, when one water molecule collides with another one, the two combining and then dissociating into a hydrogen ion and a hydroxide ion. The hydrogen ion is the H_3O^+ ion. We cannot have a proton, that is, merely the nucleus of the hydrogen atom in the water all by itself. It has to be tied up to a water molecule, so that the equation which represents the ionization of water can be represented in this way,

$$2H_2O = H_3O^+ + OH^-.$$

Because the ionization is in equilibrium, we can apply the law of mass action to it and express it mathematically by the equation,

$$K_w = [H^+]\ [OH^-]$$

where the brackets signify concentrations. At 25° C. the value of K_w is 10^{-14}, so you see that water is very little ionized. But the important thing to understand is that this equilibrium has to be satisfied wherever you have water. No matter what the solution is, whether it is very alkaline or very acid, it must be true that the concentration of the hydroxyl ions times the concentration of the hydroxide ions is equal to 10^{-14}, so that even in normal sodium hydroxide solutions, we still have some hydrogen ions, and even in the most acid solutions, we must have some hydroxide ions in order that the product of the concentrations remains constant.

It is convenient to focus our attention on the hydrogen ion and forget all about the hydroxide ion, as is the customary procedure. If we deal with solutions where the hydrogen ion concentration is very low, such as a soap solution or blood, we run into very small numbers when we have to express the hydrogen ion concentration numerically. The hydrogen ion concentration of blood, for example, is around .00000005. It is too much bother to write down all these zeros, so Sörenson, the Danish biochemist, suggested that we use a symbol called the pH to express the hydrogen ion concentration, the "p" coming from the German word "potenz" or power. The pH is the exponent or power of 10 necessary to give the hydrogen ion concentration.

For example, in blood the hydrogen ion concentration, expressed as some power of 10, would be $10^{-7.38}$. Sörensen said, in effect, "Let's call this exponent with the sign changed, the pH and talk about pH." The pH of blood is 7.38. We can define the pH, then, as being equal to the negative of the logarithm of the hydrogen ion concentration, because the logarithm of a number is the exponent that you must take 10 to in order to get the number.

It is important to note particularly that the pH is defined not in terms of the normality of the solution, but in terms of the hydrogen ion concentration which exists at the moment the measurement is made. Unfortunately, it is very difficult to determine this exact hydrogen ion concentration. If we have a strong acid, like hydrochloric acid, we can assume it to be completely ionized and say that the hydrogen ion concentration is equal to the normality of the acid; but with a weak acid, and particularly when we have a mixture of weak acids and their salts, we can no longer make any valid assumptions about the hydrogen ion concentration, nor is it usually possible to calculate the hydrogen ion concentration even if the dissociation constant of the acid is known. We must attempt to measure the hydrogen ion concentration experimentally. Can we do this by measuring the electrical conductivity of the solution? The answer is no, because there exist in the solution so many ions of different types, like sodium ions for example, which contribute to the conductance, that we cannot find out how much of the conductance is due to the hydrogen ion and how much to the other ions.

We, therefore, have to try to measure the hydrogen ion concentration by making electromotive force (E.M.F.) measurements. Such measurements represent in general the only direct method by which we can determine the hydrogen ion concentration, or hope to determine the hydrogen ion concentration.

Fig. 1 shows a standard apparatus used for measuring the pH or the hydrogen ion concentration. It involves a

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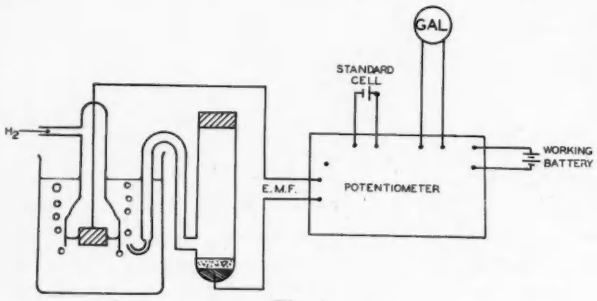


Fig. 1

hydrogen electrode, consisting of platinum, coated with an electrolytic deposit of platinum black on the surface, dipping into the test solution which is saturated with hydrogen gas. There is a salt bridge, making a liquid electrical connection to a calomel electrode, and a potentioneter for measuring the electromotive force, with a galvanometer to indicate the end point, etc.

A potential is developed on the surface of the platinum black which depends upon the hydrogen ion concentration of the solution, and as the hydrogen ion concentration of the solution increases, the electromotive force at the surface of the platinum black becomes more positive. If we put into the cell some standard solution whose hydrogen ion concentration is known, and measure the E.M.F., then remove the standard solution and put in the solution we wish to test, we can determine how much the hydrogen ion concentration has changed by measuring the change in the E.M.F.

Now, those of you who are expert in thermodynamics know that the E.M.F. is related to the concentration by a simple equation only in the ideal case of a "perfect solution," but as we never have ideal solutions, just as we never have perfect gases, we never can calculate the hydrogen ion concentration unambiguously from electromotive force measurements.

However, we might avoid this difficulty by defining the pH in terms of the so-called activity of the hydrogen ion, which is the concentration multiplied by a factor called the Activity Coefficient of just the right magnitude to validate our equations. But, those of you who are even more skilled in the science of thermodynamics realize that it is also impossible to calculate the activity of the hydrogen ion from the E.M.F. measurement, because there exists at the junction of our test sample and our salt bridge liquid, a liquid junction potential which is necessarily included in the measurement as an unknown contribution to the E.M.F. We cannot calculate this liquid junction potential because in order to calculate it, we have to know the hydrogen ion activity which we are trying to find! We do not know what we measure when we measure pH, but we do know that it is very important.

We have overcome our difficulty by adopting the practical method of measuring the electromotive force and calculating the pH number from a certain simple equation. Although we cannot say that the pH number does give us the true hydrogen ion concentration, most of us do not care. We make our pH measurements, and interpret the data in the light of the behavior of the system under investigation; in other words, we correlate the pH values with other observable properties of the solution, thus giving our pH data practical significance. Usually, we wish to know only whether our solution is more or less acid than some reference liquid, the difference being expressed quantitatively on the pH scale. To attempt to go beyond the pH to the hydrogen ion concentration is hardly ever of practical importance.

The practical difficulties of using the hydrogen gas electrode are as follows: first, the platinum surface of the hydrogen electrode is poisoned by oxygen in the air. We eliminate the oxygen on bubbling hydrogen through the solution, but it is usually difficult to get rid of every trace of oxygen and it is a tedious process. Second, the platinum surface is poisoned by many other things, such as unsaturated hydrocarbons, oxidizing and reducing agents, elements below hydrogen in the E.M.F. series, etc. Hence, we never find the hydrogen electrode used for the measurement of pH except as a standard reference electrode. If we want to check any of the Auxiliary methods, such as the colorimetric method, or the glass electrode method, we always refer it to the hydrogen electrode; but, as a practical, serviceable instrument, we never find the hydrogen electrode in use.

Another method is the colorimetric method for determining pH, and probably most of you have used this method. There are numerous commercial instruments for measuring pH colorimetrically, such as the Taylor Comparator or the Hellige Comparator, in which the color of an indicator in the unknown solution is compared with a certain standard color tinted glass slide or standard colored solution.

Soap solutions present difficulties when we try to measure their pH colorimetrically. The large soap micelle, the colloidal soap ion, may affect the indicator and change its color. Furthermore, the indicator may change the pH of the solution itself. As an example of the errors in pH readings that the indicators may give, I am going to quote from an as yet unpublished paper.[1] In the case of a solution containing 0.012 grams per liter of modified soda, sodium carbonate and sodium bicarbonate, the pH as given by the hydrogen electrode was 9.15, that given by the colorimetric method, using a Taylor Comparator, was only 7.7, while that given by the Hellige Comparator was 8.1. In the case of a soap flake solution of one gram per liter (about the concentration used in washing) the pH by the hydrogen electrode method was 10.36, by the Taylor Comparator, 9.5, and by the Hellige Comparator, 9.7, a little closer agreement.

If a stronger solution is made by adding to the soap solution 6 grams per liter of modified soda, the results come out much better, 9.83 for the hydrogen electrode,

10.0 for the Taylor Comparator, and 10.1 for the Hellige Comparator. We have here an agreement which is just about as good as you can expect for the colorimetric method. It is possible to modify the colorimetric method, using the so-called isohydric method for these very dilute solutions, to give a better agreement than that described above, but the troublesome technique of the isohydric method is made unnecessary by the availability of a simpler method for measuring pH which is vastly superior to the hydrogen electrode method or to the colorimetric method. I refer to glass electrode pH electrometers.

The glass electrode was discovered by Haber in 1909,[2] but, because of the war of 1914 to 1918, not much work was done on the glass electrode until 1920, when it was developed as a pH instrument in the physiological laboratories of University College, London.

Fig. 2 shows Haber's glass electrode. It is a very simple instrument, consisting of a bulb of glass containing within it a reference buffer solution. In Haber's case, a platinum wire from inside the bulb led to an electrometer by which the E.M.F. measurements were made with reference to the usual calomel electrode. The solution whose pH is to be measured bathes the outside surface of the glass bulb. On making the measurement, a minute current flows, passing through the glass wall, and setting up a potential between the glass wall and the solution which depends upon the pH of the solution. This glass must be of the proper composition. Usually a cheap glass is used; that is, a very soft glass such as Corning .015.

The glass electrode can be standardized by putting into the cell a solution of known pH and adjusting the reading to this pH. On removing the known solution and putting in the unknown, the change in the pH is determined by measuring the change in the E.M.F.

Fig. 2—Haber's Glass Electrode.

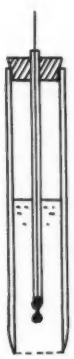


Fig. 3—Glass Electrode of MacInnes and Dole.

In Fig. 3 a glass electrode of a different type is illustrated; a very thin membrane of the special Corning .015 glass is sealed across the end of a comparatively thick-walled glass tube made of ordinary soft glass, the membrane being about 0.001 millimeter thick. Into the reference solution inside the tube is inserted a silver chloride electrode to connect the inside solution electrically with the potentiometer. From the E.M.F. developed at the outside surface, we can calculate the pH of the solution (the E.M.F. measured with reference to a standard calomel electrode). Semi-micro pH measurements have been made with electrodes of this type.

Fig. 4—A Commercial pH Electrometer

Fig. 4 shows a commercial glass electrode pH electrometer. Because of the high electrical resistance of the glass wall, the use of the glass electrode did not become widespread until vacuum tube amplifiers for amplifying the minute current that flows through the glass wall had been invented. This commercial instrument enables the pH to be measured in just about as simple a manner as possible. It is only necessary to pour the unknown solution into a glass cup, push the cup back up around the glass electrode, tap the key and move the dial until the ammeter needle shows no deflection. Then the pH is read off the dial. This instrument is just about foolproof so that untrained assistants can make a pH measurement with it.

Fig. 5 illustrates an instrument for the continuous recording of pH, using the glass electrode. The glass electrode is in a metal case, the solution flowing continuously by it. By means of the automatic recorder, we can get a continuous record of the pH.

The glass electrode has many advantages. Its surface is not poisoned by oxygen of the air, nor is it poisoned by oxidizing and reducing agents. It is not poisoned by unsaturated hydrocarbons, nor by proteins. One has to keep the surface of the glass clean, of course, but, although it is not poisoned by proteins or organic substances, it does show errors in certain cases. Furthermore, the glass electrode is fragile. If it is hit with a stirring rod, it will break, because the walls are made as thin as possible in order to cut down the high electrical resistance.

Fig. 6 illustrates a cell for the measurement of the pH of boiler water. This is shown here as it represents a cell which can be used to measure the pH without admitting oxygen or carbon dioxide of the air. In the case of dilute unbuffered solutions in which it is necessary to exclude carbon dioxide, as might be desired in measuring the pH of a soap solution, which has no buffer in it, a cell like this could be used.

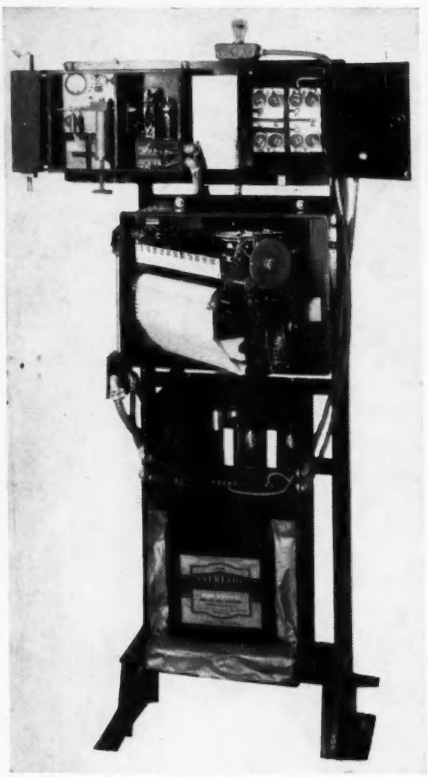


Fig. 5 — Left — Commercial Apparatus for the Continuous Recording of pH.

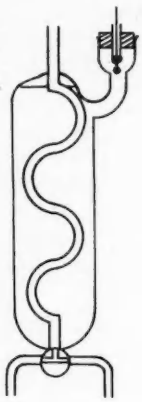


Fig. 7a—Left—MacInnes and Belcher Glass Electrode

Fig. 7b—Cameron Glass Electrode

Fig. 8 — Above—Glass Electrode of Mouquin and Garman.

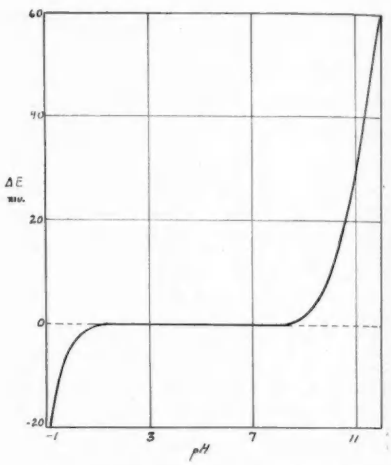
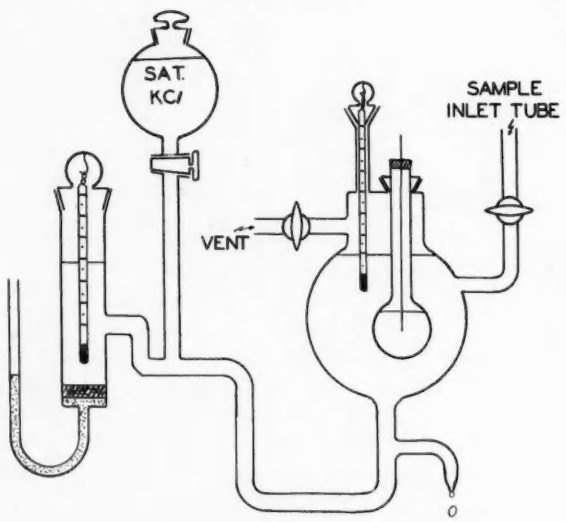


Fig. 9—General Trend of Glass Electrode Errors.



CELL FOR THE MEASUREMENT OF THE pH OF BOILER WATER
Fig. 6

In Fig. 7a can be seen another type of glass electrode which is very rugged. The spiral is made of the special Corning .015 glass which contains the sample liquid whose pH is to be measured, the liquid junction being made by means of a special stop cock at the bottom end of the spiral. The difference of potential between the inside and outside surface of the spiral determines the pH reading.

Fig. 7b illustrates an electrode invented by Dr. Cameron which enables the pH to be measured without a vacuum tube amplifier. Some Corning .015 glass is blown into the shape of a bulb and then, with a very tiny pointed flame, a small area of the bulb is heated and sucked in very quickly to give a very thin inner wall to the bulb. The inner bulb has such a large surface area, and is so thin that the electrical resistance is probably 100 times smaller. The E.M.F. developed can be measured using an ordinary potentiometer-galvanometer arrangement.

In Fig. 8 may be seen a similar electrode made by taking two small bulbs, putting them, the one touching the other, into the flame and blowing them out very rapidly so that a thin membrane divides the larger sphere. Here again the pH can be measured using an ordinary potentiometer with a galvanometer arrangement.

Fig. 9 shows the errors, ΔE, of the glass electrode as a function of pH. From a pH of about zero up to 9, the error is zero. In other words, the change of E.M.F. with change of pH would be exactly the same for the glass surface as it is for the platinum electrode. The magnitude of the alkaline salt errors depends upon the

type and concentration of positive ions present as well as upon the pH, the sodium ions giving the largest errors and the barium ions the smallest.

Fortunately, Dr. Beckman and his co-workers at the National Technical Laboratories, Pasadena, California, have discovered a glass which does not exhibit large errors in alkaline solutions, a glass which enables us for the first time to measure the pH of some alkaline solutions whose pH was hitherto unknown. In the case of a one normal sodium acetate buffer with a pH of 11.4, glass electrodes made of Corning .015 glass show errors of 36.0 millivolts, half a pH unit; whereas an electrode made of the new Beckman glass has an error of only 5.8 pH units, about one-tenth of a pH unit. Keeping the sodium ion concentration constant but increasing the pH to 13.02, the error for the Corning .015 glass rises to 96 millivolts, one and a half pH units, while the error of the Beckman glass electrode No. 4990E rises only to 14.6 millivolts.

If the solution is changed from an acetate buffer to an alkaline solution of the base tetraethyl ammonium hydroxide having a pH of 13.8, the error for the Corning glass is 35.3 millivolts, but only 2.7 for the Beckman.

These data then show that the error depends upon the pH, upon the type of positive ion present, and upon the type of glass used. The error is due to the fact that sodium or other positive ions take part in carrying the electrical current into the glass from the solution in addition to the hydrogen ion. The glass electrode acts as a hydrogen electrode because hydrogen ions only transfer the electric current across the glass membrane from one solution to the other, and since that is what happens in the case of a pair of platinum electrodes, the glass and the platinum electrodes exhibit the same electromotive behaviour; but in basic solutions, where the hydrogen ion concentration is low and the sodium concentration is high, the sodium ions take part in the electrochemical reaction and the glass electrode shows an error. But with the Beckman glass, which is probably made of lithium oxide instead of sodium oxide (although Dr. Beckman has not yet announced its composition), sodium ions presumably do not take part to such an extent in carrying the current into the glass, so the error is made less and we can use the Beckman glass electrode for determining the pH of alkaline solutions.

What is the pH of soap solutions? It varies, of course, with the temperature, the concentration, the type of soap and builder, but it is usually around a pH of 10 to 11. The alkalinity is due to hydrolysis. What do we mean by hydrolysis? The term "hydrolysis" means simply the double decomposition of a salt with water. In the case of a salt like sodium acetate, which ionizes completely into the acetate ion and the sodium ion, the hydrogen ion arising from the dissociation of water will combine with the acetate ion, since the acetic acid is a weak acid, forming a small amount of undissociated acetic acid; and as the hydrogen ions are removed from the water ionization equilibrium, more water dissociates, giving an increased concentration of hydroxide ions, and the solution becomes basic.

Hydrolysis of soaps can be represented by a similar equilibrium except that there is a complicating factor owing to the colloidal nature of soap solutions. In the case of soaps, the anion is not a simple anion, at least not at the concentrations used in washing, but it becomes colloidal; the anions agglomerate to form large particles containing many negative ions and also some positive ions; the hydrolytic equilibrium is displaced, but the soap is ten per cent hydrolyzed in the concentrations and at temperatures of interest.

The pH of salt solutions[3], illustrated in Fig. 10, is determined largely by hydrolysis. In this figure we have plotted the pH of various solutions as a function of the concentration in equivalents per liter, all the solutions, except sodium hydroxide, being basic because of hydrolysis. Sodium bicarbonate has a pH which remains practically constant with concentration above the lowest concentrations, as is the case also with borax and "modified soda," an equimolar mixture of $NaHCO_3$ and Na_2CO_3. The pH of trisodium phosphate and sodium silicate is almost as high as that of sodium hydroxide.

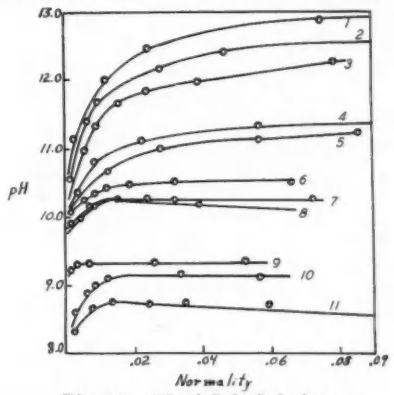


Fig. 10—pH of Salt Solutions
Curve 1, NaOH; 2, $Na_2SiO_3.5H_2O$; 3, $Na_3PO_4.12H_2O$; 4, Na_2CO_3; 5, Aqueous NH_3; 6, $NaBO_2.4H_2O$; 7, $Na_2BO_3.4\ H_2O$; 8, $NaHCO_3$ $Na_2CO_3.2H_2O$; 9, $Na_2B_4O_7.10H_2O$; 10, $Na_2HPO_4.2\ H_2O$; 11, NaH_2. All at 22° C.

Fig. 11 indicates in a general way the change of pH

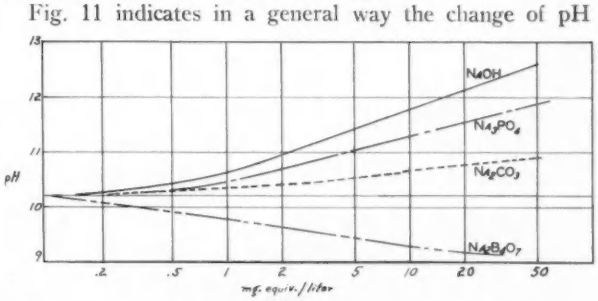


Fig. 11

of soap solutions when the so-called builders are added to the solutions. The pH of the original soap solution is

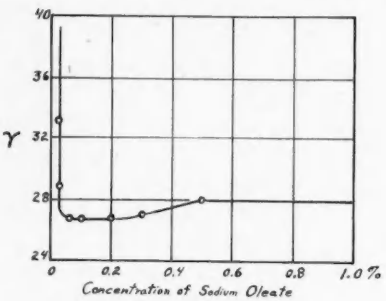


Fig. 12—Surface Tension of Sodium Oleate Solution.

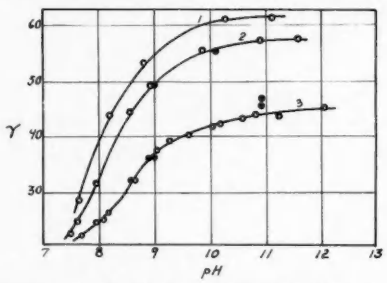


Fig. 13—Surface Tension of 0.005 *M* Sodium Laurate Solutions at 25° C. Curve 1, 0.001 *N* Phosphate Buffer; 2, 0.01 *N* Buffer; 3, 0.1 *N* Buffer.

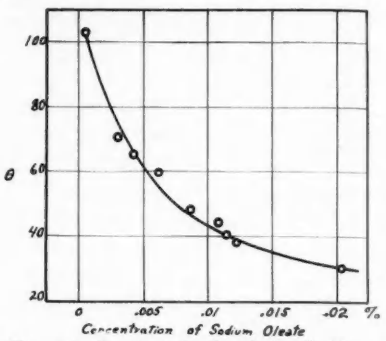


Fig. 14—Contact Angle of the Sodium Oleate Solution; Paraffin Wax, Air Interface.

between 10 and 11; in this case, about 10.2. If borax is added to the solution, the pH falls, because, as we have seen in Fig. 10, the pH of borax solution is less than 10.0. On the other hand, if trisodium phosphate is added, the pH rises, because trisodium phosphate is more hydrolyzed than soap and gives a great alkalinity to the solution.

It should also be pointed out that the pH can change quite markedly with the temperature. The pH[1] of a one-half per cent soap solution at 25° C. is 10.4; at 40° C., it is 10.0; at 60° C., it is 9.48, and at 80° C., it is 9.24, as determined by the glass electrode. Thus, it is necessary to specify the temperature in recording the pH.

Now, we should know not only the pH of soap solutions but also the alkaline capacity because there are acids in soiled clothes and unless we have a large enough reservoir of alkalinity to neutralize the acids, the solution will become acid because of these acids.

The presence of acids in dirt is indicated by some results published by Snell[4] on the number of moles of alkali removed from the soap by the acids in the soiled cloth. During the first washing, 0.005 of a mole per litre was removed; in the second wash, 0.0024; in the third, 0.0022; and in the fourth, none, showing that all the acid had been removed from the clothes by the three washings. One wonders if the cloth removed some of the soap from the solution by adsorption, and thus changed the alkalinity. However, this effect, if it existed, would not alter the conclusion that clothes soiled with dirt and grease contain acid which must be neutralized. We should have then an alkaline builder in soap solutions to maintain the alkalinity as the washing process proceeds; otherwise, the acids in the dirt will lower the pH of the solution.

How does the surface tension of soap solutions vary with the pH? In Fig. 12 the surface tension of a soap solution is plotted as a function, not of the pH, but of the concentration of sodium oleate[5]. When the concentration of the sodium oleate reaches 0.05 to .1 per cent, the surface tension drops rapidly; this is the concentration used in washing, as it should be, because a low surface tension means a low contact angle, and detergent properties depend upon having a low contact angle between the solution and the grease or dirt, or whatever has to be cleaned.

Fig. 13 illustrates the change of surface tension with change of pH, as published recently by Harkins and his co-workers[6]. It is interesting to note that the surface tension rises as we make the solution more alkaline. This also means that if we put in alkaline builders to maintain the pH constant or to increase the pH to 10 or 11, the surface tension is increased, which is not desirable. The reason for this increase in surface tension is due, probably, to the fact that the addition of the alkaline reagents neutralizes the free fatty acid in the soap solution which was partly responsible for the original lowering of the surface tension. It is extremely interesting to note that while the top curve was obtained by increasing the pH by adding 0.001 phosphate buffer, the data represented by the solid circles in the lowest curve was obtained by simply adding sodium chloride, or salt, to the 0.001 normal buffer—soap solution. In other words, in this case the drop in surface tension from that of a solution, let us say, having a pH of 10 in the .001N buffer down to that for the salt-buffer solution of the same pH was due simply to adding the salt, sodium chloride. The explanation is as follows: The colloidal micelles that are formed in the soap solution are prevented by electrical forces from rising to the surface of the water in the dilute solutions, and (It will be recalled that the lowering of the surface tension results from the accumulation of soap at the surface.) so the surface tension is high. But if we add salt, the electric forces are diminished because of the greater conductivity of the solution, and the soap micelles can become adsorbed in the surface, thus lowering the surface tension.

In Fig. 14 we can see how the contact angle between the solution and, in this case, paraffin, changes with the concentration of sodium oleate. The contact angle is the angle that the water-air, or the solution-air interface makes with the paraffin-solution interface and, for complete spreading of the water over the grease, the contact angle should be zero. It is necessary to have a low contact angle for high detergent action. It can be seen that dissolving the sodium oleate in the water has an enormous effect on the contact angle, even at a concentration of 0.02 per cent the contact angle has declined below 40°.

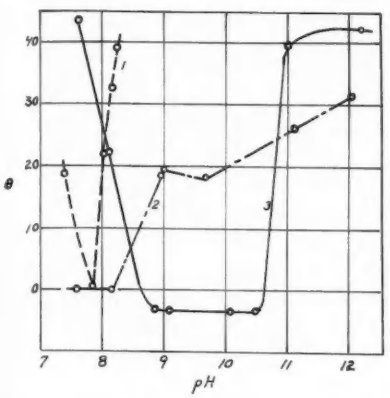


Fig. 15 — Curve 1, Contact angle for 0.1% sodium laurate on paraffin; 2, 0.1% sodium laurate on wool; 3, 0.1% sodium oleate on paraffin. pH regulated by 0.25% phosphate buffers.

At this angle the solution wets the paraffin, but the contact angle must fall nearly to zero before the solution will spread over the grease.

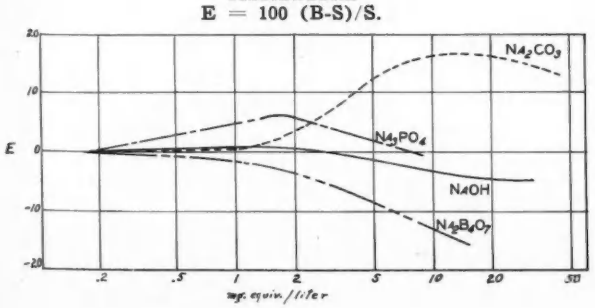
In Fig. 15 the contact angle, Θ, is plotted as a function of pH. The solid line is the curve for a 1/10 per cent sodium oleate solution on paraffin, and it can be seen that when the pH rises to 8.8, the contact angle has dropped to zero. From a pH of about 8.8 to 10.5, the contact angle remains zero, but as the pH rises above 10.5, the contact angle rapidly rises. In the region 8.8 to 10.5 the contact angle is, therefore, not sensitive to pH.

Other soaps have a different behavior, as might be expected. Sodium laurate in 0.1 per cent solution gives the dotted line which does not have the broad minimum exhibited in the case of sodium oleate solutions.

Furthermore, the contact angle also depends upon the solid substrate; thus the contact angle for a 0.10 per cent sodium laurate solution on wool is an entirely different function of the pH from the curve for paraffin as the substrate. Incidentally, it is possible to calculate the shape of this curve theoretically, assuming that Antonow's Rule holds for solid-liquid interfaces as well as for liquid-gas interfaces.

Detergency as a function of pH has been studied by Rhodes and Bascom[7] who expressed their data in terms of B, the change in brightness after five washings for a soap solution to which a builder has been added, and S, the change in brightness after five washings for a pure soap solution. By referring to Fig 16 it can be seen that

Fig. 16—Change in brightness as a function of soap builder concentration.
E = 100 (B-S)/S.



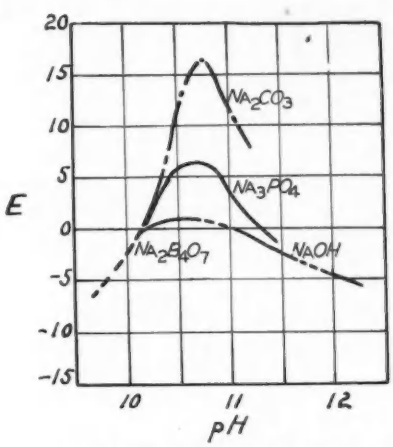


Fig. 17—Change in brightness as a function of pH.

adding borax decreased the brightness, that adding sodium hydroxide also decreased the brightness, but that on adding trisodium phosphate and sodium carbonate, the brightness increased, reached a maximum and then fell off as the concentration increased.

These curves seem to show no relation to each other, but if we study Fig. 17, in which the function E is plotted as a function of the pH, we see that a maximum in the detergent power, at least as measured by these authors, is obtained at a definite pH of 10.7. The maximum for each solution occurs at the same pH. In the case of sodium borate solutions, the brightness fell; the pH of this buffer solution is less than the pH of the pure soap, so that as borax is added the pH falls, giving the extension of the curve to the left in Fig. 17. It is interesting to note that this extension seems to fit in quite well with the other curves.

These data indicate that there is a definite relationship between pH and detergency. We should remember, however, that the total alkaline capacity of the soap solution, which can be measured only by titration, is also important.

DISCUSSION

Chairman Boxser: On that last slide you have the optimum pHs giving you the best brightness. From my contact with laundries, it appears that sodium hydroxide is a favorite builder of soaps for getting whiteness, that is, the maximum whiteness in clothes. According to these curves, sodium hydroxide does not seem to give the greatest brightness.

Dr. Dole: Sodium carbonate does, but there is also the possibility of using metasilicate which has a high ratio of base to silica.

Chairman Boxser: This was before the days of metasilicate. Years ago we hardly saw a laundry using anything else but caustic soda and soap. They used to use various other alkaline builders, but that combination seemed to be the favorite. If they had dirty clothes and

they wanted to get them white quickly, they used caustic soda and soap. Of course, meta-silicate helps a whole lot, but you hardly see them use soda ash.

Dr. Dole: Of course, there are some substances like trisodium phosphate which, when dissolved in water, will remove oil and grease, although they are not soaps, because the contact angle is lowered sufficiently so that the water can work its way under the grease and remove it.

Chairman Boxser: That is also true of caustic soda.

Question: Would you mind going over your explanation again as to why it was that sodium chloride added to a mixture of soap and buffer at pH 11, lowered the surface tension?

Dr. Dole: Consider a positive ion like a sodium ion and imagine it to be brought from a vacuum or from air into water; in this process there is liberation of an enormous amount of energy, about 100,000 calories per mole, which is the hydration energy of the positive sodium ion. In other words, ions have a great tendency to become completely hydrated, or to become completely buried in water. Now, in the case of solutions of a soap, like sodium palmitate or sodium oleate, we have large colloidal particles, negatively charged, and these micelles, being rather insoluble in water because of the hydrocarbon chains, tend to rise to the surface to become adsorbed on the surface, whereas their "gegenions" or "counter" ions, as they say in colloid chemistry, like ordinary ions are repelled from the surface. We have two tendencies, the sodium ions trying to move away from the surface and the micelles trying to reach the surface. These opposing forces produce a smaller adsorption of micelles on the surface than would exist if the micelles could migrate freely to the surface, but if the concentration of sodium and chloride ions is increased, the electrical force decreases because of the increased conductivity of the solution, and the micelles can then more freely go through the solution. In this way the micelles will rise to the surface to a greater extent and produce a greater lowering of the surface tension.

Question: About what is the magnitude of the salt concentrations that bring about these noticeable effects in the surface tension?

Dr. Dole: By referring to Fig. 13 it can be seen that a salt concentration of 0.1 N brings about a pronounced lowering of the surface tension.

REFERENCES

[1]Unpublished material of Bacon, Hensley and Vaughn.
[2]For a complete discussion of pH and the glass electrode see the author's forthcoming monograph, "The Glass Electrode," to be published by John Wiley & Sons, Inc., N. Y.
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[4]F. D. Snell, Ind. Eng. Chem. 24, 76 (1932).
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[7]F. H. Rhodes and C. H. Bascom, Ind. Eng. Chem. 23, 778 (1931).

Finishing Treatments—

(Concluded from page P230)

are thus closely related because it is the small differences or variations which need to be controlled. In case fabrics of different types are being tested to find the one most suited to a given use, that method which best measures this quality should be used.

The Drapeogram has been discussed in Part IV, pages 471-472. Its permanent, visual records made at the time of the test gives a stiffness picture immediately comprehensible in a manner that figures cannot accomplish except for the experienced observer. At the same time the chord length may be measured directly from the Drapeogram and used in reports or for mathematical analysis.

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PUBLICATIONS AND TEST MATERIALS, WITH PRICES

American Dyestuff Reporters

Back numbers less than 2 years old can be obtained from Howes Publishing Co., 440 Fourth Ave., New York City; earlier numbers from the Secretary of the Association, Lowell Textile Institute, Lowell, Massachusetts. Prices postpaid: 50c each to non-members, 35c to members; complete volumes $5.25 to non-members, $4.50 to members.

Year Books

From the Secretary, Postpaid

Current volume, to non-members, $3.50; to members, one extra copy per member $2.50. Back numbers, to non-members, $1.50; to members, $1.00.

Reprints from the American Dyestuff Reporter and Year Book

From the Secretary, Postpaid

Light Fastness Reports, I, II, III, bound together	$1.00
Light Fastness Reports, I, Series 3	.20
Light Fastness Reports, IV	.30
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Wool Carbonization, I, II, III, Sulfuric Acid	.50
Wool Carbonization, IV, V, VI, Sulfuric Acid and Aluminum Chloride	.50
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Printing Pastes, Preliminary Report	.40
Vat Printing Pastes, I	.40
Vat Printing Pastes, II	.40
Extraneous Matter in Textile Materials	.50

Reprints of Researches by the Association at the National Bureau of Standards may be obtained from the Superintendent of Documents, Washington, D. C.

Materials for Tests

From Chairman of A.A.T.C.C. Research Committee, Lowell Textile Institute, Postpaid

Knitted Worsted Tubing, under fifty yards, per yard	$ .23
fifty to ninety-nine yards, yer yard	.20
100 yards or more, per yard	.18
Washing Fastness Standards, Cotton, per set	1.00
Wool, per set	1.00
Silk, per set	1.00
Light Fastness Standards	1.00
Rubbing (Crocking) Fastness Standards	1.00
Crock-Meter Cloth, per package	.20
3 packages	.50
7 packages	1.00
Crock-Meters, from W. C. Durfee Co., 114 Federal St., Boston, Mass.	12.50
Counter, attached, additional	6.00

Launderometers, from Atlas Electric Devices Co., 363 West Superior St., Chicago, Illinois.

• TECHNICAL NOTES FROM FOREIGN SOURCES •

Modern Textile Finishing Machinery

K. S. Laurie—J. Soc. Dyers & Col., 56-298, *July*, 1940.—From the engineer's point of view, the processes of finishing may be summarized as (a) drying; (b) impregnating; (c) control of dimensions and (d) production of surface effects. In the past, machines made for these purposes have been relatively crude and simple, although effective. The present paper deals with certain modern developments in such machinery, particularly as concerns the drying operation, and the author points out that the finisher of today can rely on the textile engineer to produce machines embodying the most modern engineering ideas and refinements, and suitable in every way for his requirements.

It may be taken as a principle that, so far as it is possible to do so, it is cheaper commercially to remove moisture by mechanical methods than by applying heat. The finisher's appliances for the mechanical drying of cloth are the mangle, the hydro-extractor and the open width or suction extractor. Of the three, the mangle is cheapest in power cost and the suction tube probably the most expensive. Any of the three methods may leave the cloth with a moisture content of between 100 per cent and 60 per cent by weight, compared with the dry cloth. The remainder is practically impossible to remove mechanically, and recourse must be had to other methods.

The simplest form of cloth drying machinery, and the cheapest to operate, is the set of revolving steam cylinders round which the cloth passes, giving up its moisture as it moves forward. This method of drying, however, though comparatively efficient, is by no means suitable for all types of fabric. It exercises little or no control over the dimensions of the cloth, either in width or in length, and in such materials as silk and rayon definitely hard and harsh surfaces result from cylinder drying. The cylinder machine is therefore seldom used for final drying, and on some cloths cannot be used at all.

The alternative cloth dryers are the large group of machines which utilize a hot air stream to absorb and remove moisture from the cloth. Though this method is not so efficient as cylinder drying, the commercial advantages in respect to improved finish and dimensional control more than outweigh the extra cost of heat and the increased complication of the machine. The Festoon Machine or Hanging Dryer was the most obvious development of this principle. As in this machine the cloth moves forward in unsupported loops hanging from poles it is obvious that only comparatively slow air velocities can be employed. Its rate of output is therefore low for its bulk and steam consumption.

Various attempts were made to give better support to the cloth so that a higher air velocity could be employed. The creeper type of dryer, consisting of several layers of travelling lattice or netting on which the cloth rests while being blown on by traverse air streams, gives excellent qualities of finish, but still the cloth is insufficiently firmly supported to allow of high air velocities and a high output. In the Buti or drum type dryer the cloth lies on a blanket which is supported on a perforated steel shell covering the revolving drum which is enclosed in an outer casing through which the cloth is fed. Hot air is blown into the casing and extracted from inside the revolving drum after passing through cloth and blanket. This dryer gives excellent results with light and delicate fabrics, and is probably unique among practical dryers in that the air stream is forced to pass through the cloth.

Both experimental work and theoretical considerations have led to the view that the conditions for effective moisture absorption, at any given temperature, are analogous to those for efficient heat transference. That is, there must be an effective scrubbing action between the air and the cloth, a combination of high relative velocity and of fine state of division of the air stream, so that as large as possible a proportion of the air particles comes into intimate contact with the moisture in the cloth. Passing air through the cloth gives intimate contact, but the amount of air that can be so passed is small. Blowing air at the cloth in large streams is effective, but its effect is local and is apt to put a considerable strain on the cloth. Blowing air streams along or across the surface is ineffective. The most modern and effective method is that of dividing the air streams into small high velocity jets, closely spaced, which impinge on the cloth at close range without loss of velocity. The cloth is either supported against a lattice or is partly balanced by similar jets of air playing on the other side of it exactly opposite to the first.

One of the simplest drying machines incorporating the air jet system is the Spooner vertical dryer. In this the cloth passes up between one set of opposed nozzles and down between a second set, being then delivered to a folder. The Proctor Multipass Airlay Dryer has been developed to meet the conditions of high output combined with gentle handling of delicate fabrics and full freedom to shrink the cloth if required. Here the cloth rests on the flat cork surfaces of poles which are carried up and down in nearly vertical passes by a pair of conveyor chains. Fine jets of air are blown from slots onto one side of the cloth, and hold it against the cork faces as well as drying it. A considerable length of cloth is thus subject to effective drying conditions in a comparatively small bulk of machine, and owing to this feature the Airlay dryer gives a great output per sq. ft. of floor space.

The most complete and versatile cloth finishing machine is the stenter, since, in addition to drying, it controls the width of the piece, and in some machines the length also. There follows a fairly detailed description of various types of stenters and stenter chains, including the special uses

for which the pin link, the spring clip and the automatic clip are employed. It is noted that in recent years the requirements of poplin makers for shrunk fabrics and of the rayon trade for dimensional control have caused a revival of the old type pin stenter, now equipped with various modern improvements. The heating of stenters shows a similar variety of arrangement and system to the heating on other drying machines. Most existing clip machines have "puffer" type heating, the hot air being blown onto the cloth in large streams from nozzles. Some of the older pin stenters and occasional special clip machines are heated merely by radiation plus convection from steam pipes lying under the cloth. The more modern machines are being equipped with some type of close-jet heater, and outputs up to double those of the older type are often obtainable in a given length of machine.

The article, which is illustrated with numerous excellent photographs and diagrams, concludes with a description of various modern feed and delivery devices for stenters, and mentions in passing the photo-cell controlled weft straightener which has been developed in America.

Another Test for Wool Oils

W. Garner and M. Elsworth, Analyst 65, 347, 351, 1940.—When 3 per cent of olive oil is spread on wool as a lubricant for combing, one pound of the oil becomes distributed more or less completely over a maximum surface of about half an acre. (A pound of the wool fiber has a surface area of about 70 square yards.) This condition is very favorable to rapid oxidation although Garner states in a later publication that in spite of such favorable conditions only about 20 per cent of olive oil on wool becomes oxidized in two weeks after combing.

Oxidation of any wool oil should form only products which are pale in color and easily scoured out but, as is well known, if conditions are not favorable, resinous or paint-like polymers may result which are yellow or brown and difficult to remove with alkaline soap. Oxidation may be so rapid as to cause spontaneous combustion. However, "The rate of oxidation gives no indication of the type of oxidation product and depends far more on the amount of certain types of impurities than on chemical constitution." (Garner in J. Soc. Dyers and Colourists 56, 335).

There are four main factors influencing the rate of oxidation of a non-drying oil, viz.: (a) ratio of oil surface to amount of oil (thinness of spreading); (b) the activity of oxidizing catalysts present; (c) the activity of antioxidants; (d) the temperature conditions. As already implied the chemical constitution of the oil is of "very minor" importance, especially in comparison with the catalyst-antioxidant balance.

The value of an oil for wool lubrication cannot be predicted from the usual analytical data such as iodine value; and the Mackey test is not any too satisfactory. In fact Garner says that any wool oil can be made to give any desired result in the Mackey test. The heating in this test comes probably from peroxide formation and decomposition, these reactions being promoted by rise of temperature.

The work under discussion was based on the idea that the rate of accumulation of peroxides when an oil is exposed to the influence of light and air should be a measure of the effective activity of the oxidizing catalyst present. The actual peroxide content of an oil does not tell the story because the previous history is usually unknown. Such peroxide may have resulted from either slow action for a long time or from quick action due to high catalytic activity. The peroxide content refers to something that is past while the measure of the peroxide accumulation rate (P. A. R.) indicates the probable rate of oxidation of the oil in the future.

Apparatus and method are described for testing oils under an electric light whose heat is absorbed by running water. The P. A. R. is determined from the peroxide content of the oil before and after exposure. Various details and sample values are given together with additional points on wool oils. The peroxide iodine value alone is regarded as almost useless for evaluating oils.

Wool oils should be considered from two nearly unrelated aspects: (a) rate of oxidation, which depends upon the balance between catalyst and antioxidant; (b) type of end product, depending upon amounts of unsaturation. The first is clearly indicated by the P. A. R., high values going with unsatisfactory Mackey tests and with rapid oxidation when used on textiles. The P. A. R. does not indicate the amount of catalyst nor the type of end product. The latter may be checked by the alkaline ageing test reviewed in the American Dyestuff Reporter of August 19, 1940, page 416.

Antioxidants are not a complete answer to wool oil problems. Those of the amine or phenol type are liable to yield colored oxidation products which can stain textiles, and as soon as an antioxidant is exhausted the oil will begin to oxidize in its normal manner. Cotton seed or linseed oil stabilized by beta-naphthol give good results in the P. A. R. and Mackey tests but are not suitable oils for wool. Olive oil containing large amounts of catalysts might be thus stabilized but would not be a good oil. An antioxidant merely slows up the oxidation but does not change the ultimate nature or end products of the reaction.

The P. A. R. agrees qualitatively with the Mackey, normal oxidation, and ageing tests; and seems to yield the same kind of information as the Mackey test. Both show up bad oils but are not dependable in indicating good ones. A good result may mean a good oil free from oxidizing catalysts, or it may indicate merely that the catalysts are masked by antioxidants. The test represents one more valuable method of contributing to a knowledge of oils for wool.

Testing Wettability of Fibers

Blow and Moxon, J. Soc. Chem. Ind. 59, 171, 1940.—Owing to the present great interest in various phases of the wetting of textiles, attention is called to a new method which has been devised for determining the wettability of textile fibers and has been tried first on wool yarn. Its purpose is to provide a method of comparing the ease or difficulty of wetting textile fibers without various complications such as that of fabric structure.

Wool was taken as being particularly adapted to such an investigation because various samples differ widely in wettability and, of course, some treatments affect this property. Instead of exposing a fabric to penetration by water under definite conditions of pressure, the authors replace the fabric with a brass plate, containing a plug of yarn drawn through as a bundle of threads and cut off with a microtome knife. The plate is 5/16 of an inch thick, drilling with a quarter inch hole for the plug of yarn. Methods are described for forming the plugs.

Two factors determine the pressure required to force water through the plug, which is a capillary structure. One is the size of pore or cross section of space within the plug. This is checked for uniformity from one experiment to another by a determination of air permeability, with possible limitations when comparing different wools. The other factor is the interfacial tension between water and fiber which can be measured as wettability as soon as the pore size factor is defined.

Various precautions are necessary because pore size in the plug can vary with humidity and regain so that the air permeability may be misleading. The pressure required to cause penetration by water is not so sensitive to moisture content of the fibers.

With different yarns from one lot of wool the weight of wool in the plug determines the air permeability and water penetration. Count and twist has no significant effect. Dyeing and different ways of scouring, however, had considerable and varied effects, dyed yarns being rather less wettable.

The ordinary wool fiber itself is considered to be of low wettability. The precipitation of calcium and magnesium compounds contributes to the differences between scoured wools. Chemical treatments to make wool unshrinkable e. g. chlorination, may increase the wettability. The Velan (Zelan) treatment reduces it as, of course, it should.

The work reported so far is only preliminary, to establish the principles of the method.

TRADE NOTES • NEW PRODUCTS

OBITUARY

C. G. V. SJOSTROM

CARL G. V. SJOSTROM, president of the C. G. V. Sjostrom Co. of Springfield, Mass., died on April 11th at the home of his daughter in North Wilbraham. He was 82 years old. He had been a resident of Ware for 40 years and had moved to North Wilbraham but recently.

C. G. V. Sjostrom

He was born in Stromfors, Sweden, and his family moved to Sherbrooke, Canada when he was 10 years old. He was educated in the public schools at Sherbrooke and St. Francis College, Richmond, P.Q. He then entered the employ of the Paton Mfg. Co. and was taught the art of dyeing under the tutelage of his father. In the early eighties he came to the United States and took his first position as overseer of dyeing with the Ed. Harris Woolen Mill in Woonsocket, R. I. In 1885 he was with the Valley Worsted Mills in Providence, R. I., and in 1894 he started the Lawrence Dye Works in Lawrence, Mass. in association with his father. This later became a division of the United States Worsted Mills. After selling out his interest in the dye works he accepted a position with the Geo. H. Gilbert Mfg. Co. of Ware, Mass. In 1919 he resigned this position and, with his son F. L. H. Sjostrom, started the C. G. V. Sjostrom Co. in Springfield which engaged in the manufacture and distribution of dyestuffs, chemicals, and specialties and he acted as a consultant on dyeing and finishing problems. One other son, Raymond B., later became associated in the business.

He was a charter member of the American Association of Textile Chemists and Colorists. He was also a member of the Drysalters' Club, Engineers Club, Masons, Shriners, and the Springfield Rotary Club.

He is survived by a daughter, three sons, two brothers, one sister, and three grandchildren.

• RAYON INSTITUTE

A Rayon Institute will be conducted at North Carolina State College Textile School during the week of May 5-9. Outstanding men in the rayon industry will deliver a series of lectures which will be open to anyone connected with the textile industry. No registration fee or any other charge will be made as this will be a service offered to the trade by the School. Following is a list of those who will take part in the proceedings and the subject that each will discuss:

Dr. Harold DeWitt Smith, of A. M. Tenney Associates: "Recent Developments in Synthetic Fibers and Fabrics."

C. R. Hall, Weaving Technician, Enka Corporation: "Methods of Testing Synthetic Yarns and the Relation of Testing to Problems of Production in the Mills."

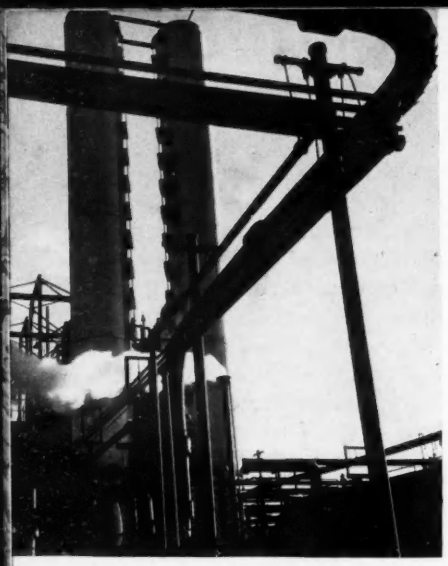
H. B. Summerell, District Supervisor and Technician, North American Rayon Corporation: "Current Practices in Rayon Warp Preparation and Weaving."

H. O. Kennette, Technical Sales, E. I. du Pont Company: "Growth of Spun Rayon and Its Processing in the Mills."

D. L. Friday, Manager, Cocker Machine & Foundry Company: "Rayon Slashing."

Irvin Lewin, Manager, Carter Fabrics, Inc.: "Development of the Rayon Industry from the Viewpoint of a Practical Mill Man."

Frank Love, Chemist, North American Rayon Corporation: "Problems Commonly Met in Dyeing and Finishing Rayons."



A View of Calco's Light Oil Plant, from the Book "Dyes Made in America."

● HISTORY OF AMERICAN DYE INDUSTRY

In conjunction with the celebration of its twenty-fifth anniversary, Calco Chemical Division, American Cyanamid Company has prepared "Dyes Made In America," a study of the development of the American dyestuff industry. The thread of this narrative, written by William Haynes, formerly publisher of Chemical Industries, commences with the critical shortage of chemicals facing this country in 1915. The British blockade created a famine in dyes, bulk chemicals, and pharmaceuticals.

"Dyes Made In America" describes the early beginnings of Calco, how they succeeded by painstaking experiments to make aniline oil, beta naphthol and finally such dyes as methylene blue, crimson and tartrazine.

How completely the German Cartel had succeeded in dominating the chemical industry is described by "Dyes Made In America." It is stated that by controlling the methods of manufacture, and by adroitly constructing a price structure that bypassed the American tariff, the Cartel had prevented the development of an organic chemical industry in this country. The book describes the work of the late Francis P. Garvan, World War Alien Property Custodian, in helping to break this German throttle-hold and in intelligently guiding the post-war growth of America's new chemical industry.

One illusion shattered by Williams Haynes' account in this book is the notion that the dye industry in this country was nursed into being by the especially benevolent protection of a paternalistic policy of the U. S. Government. The bitter disappointments, the back-breaking struggle, the brilliant accomplishments of American research—all these are placed in their true perspective by this volume.

"Dyes Made In America" presents a conception of the manufacturing efficiency of American producers in a manner probably not presented heretofore. It is stated that the synthetic colors supplied to the textile industry and other users here are unequalled for tinctorial strength, purity, and uniformity.

American dye users, the writer asserts, have learned that the true cost of a dye depends quite as much upon its concentration as upon its price per pound. Stronger colors mean greater convenience and economy in application, more uniform and satisfactory results. Also, the weighted average price of all American dyes has been brought from $1.26 per pound in 1917 down to 55c in 1937.

Calco's book has been splendidly prepared. It is illustrated with a number of half tones of industrial production and also a series of natural color photographs showing the application of American-made dyes. These photographs, hand mounted for artistic effect, show a wide assortment of textile fabrics including woolens, cottons and rayons.

● APPOINTS WASHINGTON REPRESENTATIVE

The Drug, Chemical and Allied Trades Section of the New York Board of Trade has appointed Carson Gray Frailey, Albee Building, Washington, D. C., to handle certain Section affairs pertaining to the Federal Government.

John J. Toohy, Chairman of the Section, in making the announcement said: "I feel confident our members will welcome the appointment of Mr. Frailey and will find his services most helpful because of his wide acquaintanceship in Washington and his thorough knowledge of industry problems."

Mr. Frailey is a graduate of Johns Hopkins University, holds a Law Degree from the University of Maryland, and is at present lecturing on pharmaceutical law at Temple University. He has already taken up his new duties.

● SPRING CATALOG

The new Spring 1941 catalog of the Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y., contains many important new titles. Books of importance in all technical and scientific fields, and to National Defense, have been added to the previous standard authoritative works.

A glance through this new catalog reveals books of interest to the chemist, pharmacist, engineer, scientist, architect, aviator, metallurgist, technician, machinist, farmer, advertiser, home gardener, etc.

A new format makes the catalog easier to read. The convenient classification, extended table of contents, and index, all assure the quick location of specific titles and subjects. Upon receipt of a 3c stamp to cover postage, a copy of this catalog will be sent free of charge.

● ANHYDROUS AMMONIA

A new booklet entitled "Mathieson Anhydrous Ammonia" has recently been announced by The Mathieson Alkali Works, 60 East 42nd Street, New York, N. Y. The book is sixteen pages and cover and measures 6" x 9".

Some of the subjects covered in detail are the chemical and physical properties of liquid anhydrous ammonia, including curves on pressure and temperature relations, density of liquid ammonia and solubility of ammonia in water; ammonia containers and their safe handling; withdrawing ammonia from containers and from the system; piping and valves; ammonia leaks; physiological effects of ammonia; and first aid measures in case of serious injury or exposure.

Copies of this new Mathieson booklet are available to consumers upon request.

● TESTIMONIAL DINNER

Friends of Ralph Hart gave him a surprise testimonial dinner at the Sky Gardens, St. Moritz Hotel, New York City, on Sunday, March 23rd. The event was unusual in that there was no specific date, anniversary or "what-have-you" to celebrate. It was a spontaneous gathering of friends of Mr. Hart as a tribute to a "Genial Host, Good Friend and All 'Round Regular Guy." Among the more than 100 guests present, were many prominent in the textile industry.

● MEETING, S.C.I.

A meeting of the American Section of the Society of Chemical Industry was held on April 18th at The Chemists' Club, 52 East 41st Street, New York City. This was a joint meeting with the American Institute of Chemical Engineers and the New York Section of the American Chemical Society. The Chairman, Dr. Lincoln T. Work, presided.

Dr. Alexander Silverman, the speaker of the evening, spoke on the subject "Glass: Today and Tomorrow." The newer developments in plate and window glass manufacture, bottles, illuminating ware, optical glass, fiberglass, and art glass were discussed. In connection with plate and window glass, demonstrations were given of the newer types which are employed for safety and for the absorption or transmission of special radiations. Fluorescent lighting and the use of ultra-violet and sodium vapor light were considered as to illumination, sterilization, and tenderizing. The importance of art and the application of glass to things artistic were stressed. The lecture was made particularly interesting by illustrations with colored slides, specimens, and experiments.

● COLOR PRINTS

By means of standardization on 35 mm. and Bantam size Kodachrome transparencies and a standard 8″ x 10″ print size, Color Prints, Inc., 1711 North Vermont Avenue, Hollywood, Calif., state that they are able to produce genuine wash-off relief, 3-color prints on paper, individually balanced, for $3.00 per print. Additionally prints can be had from the same negative for $1.00 per print if ordered within 60 days. Further information is available upon request.

● PURCHASE PROVIDENCE DRY-SALTERS DIVISION

Announcement has been made by Arnold, Hoffman & Co., Inc., Providence, R .I., of the purchase from Hercules Powder Co. of its Providence Drysalters Division located at East Greenwich, R. I. This will be consolidated with the A-H manufacturing facilities at Dighton, Mass. This purchase enables Arnold, Hoffman to offer a variety of additional products such as Concental, Mellol, new soluble pine oils, and various new rayon oils. Former customers of the Providence Drysalters Division are advised that all contracts made with them for products manufactured at East Greenwich will receive the same careful attention to detail, uniformity, and prompt service to which they have been accustomed. Walter R. Bunce, formerly with Hercules Powder Co., is now with Arnold, Hoffman.

● GENERAL RELEASES

General Dyestuff Corp., 435 Hudson Street, New York, N. Y., announces release of circulars describing the following products:

Palatine Fast Red R N A—an acid dyestuff which is said to possess fastness properties closely approaching those of the chrome colors. It is said to be well suited for producing fast-to-wearing shades on the better grades of ladies' and men's wear. It can be used on piece goods and on yarns of all kinds, especially knitting, hosiery, and carpet yarns, and further, on loose wool and slubbing which is to be given a light fulling. It is suited also for producing fast shades on silk. It can be discharged to a good white with Rongalite C on either a wool or a silk ground. Circular G-238.

Monochrome Black Blue G A—a chrome color said to possess many valuable properties. It may be applied by either the afterchrome or monochrome method. It is said to produce shades of very good fastness to light, washing, fulling, water, salt water, and perspiration. It is further said to be particularly useful where fastness to light and to fulling is required on loose wool, slubbing, piece goods, and yarns. It is stated that, due to its good level dyeing properties, it is well suited for dyeing fast mode shades in combination wtih Acid Alizarine Flavine R A or Chrome Yellow A Extra and Monochrome Red F G A Conc. Circular G-239.

Para Yellow F R A Conc.—a direct dyestuff which produces reddish shades of yellow when coupled with Nitrazol C F Conc. It is well suited for dyeing cotton or rayon, both piece goods and yarn, and produces shades said to be of fairly good fastness to washing, good fastness to water, and very good fastness to perspiration and to hot pressing. It can be discharged to a good white with Rongalite C. The dyeings are said to form an excellent ground for discharge styles which must withstand washing. Circular G-240.

Diamond Black P V Conc.—a chrome color producing full and bloomy shades of black said to possess excellent all around properties. It is stated that it is largely used for the dyeing of loose wool, slubbing, piece goods, and yarn wherever the best fastness properties are required, especially fastness to fulling, to potting and to cross dyeing. Circular G-241.

Monochrome Violet F B A—a chrome color recommended by the manufacturers for the production of straight shades of a bright violet and, likewise, as a shading color in combination with other chrome dyestuffs. The dyeings are said to be distinguished by very good fastness to washing, to fulling, to water, to sea water and to perspiration. It is stated that it is suited for dyeing loose wool, slubbing, piece goods, and yarns. It can be dyed either by the monochrome or the afterchrome method. Circular G-242.

● CALCO BULLETIN

A Technical Bulletin on U. S. Marine Corps Uniform Cloths of Wool has been issued by the Calco Chemical Division, American Cyanamid Company. This bulletin gives information concerning the dyeing of wool for the following Marine Corps uniforms: flannel—13-oz. green; kersey—16- and 22-oz. green. Similar information is given in this bulletin for dyeing Marine Corps blankets and blanket heading. These data include dyes that may be used for these materials, the formulations for these dyes, the proper mixes and suggested methods of dyeing. Copies may be obtained from Calco by asking for Technical Bulletin No. 593.

● CYANAMID BOOKLETS

American Cyanamid & Chemical Corp., 30 Rockefeller Plaza, New York, N. Y., has recently released a booklet entitled "Quadrafos (Sodium Tetraphosphate)" which describes its composition, properties and uses. The product is said to effectively soften water without precipitation and consequently is finding a rapidly increasing industrial use. This property of Quadrafos is of especial importance in textile wet processing and a detailed presentation of its application in this field is given. Among the processes in which it is of value are the following: *cotton*—kier boiling, bleaching, dyeing, back filling, sizing and finishing; *wool*—scouring, piece goods scouring and dyeing; *rayon*—throwing, boil-off, dyeing and finishing; *silk*—removal of insoluble soaps resulting from the soaking of silk yarns. It is stated that Quadrafos may be used without harm to the fiber and will result in more efficient operations.

Also newly published is a revised edition of Cyanamid's catalog "Industrial Chemicals."

Copies of both of these publications are available upon request.

● MEETING, A.A.T.T.

The next meeting of the American Association of Textile Technologists will be held on May 7th at the Building Trades Employers' Association, 2 Park Avenue, New York, N. Y. The speakers will be: Dr. Henry D. Evans, Pepperell Mfg. Co., "Function of a Testing Laboratory in the Textile Mill" and Dr. Milton Harris, Research Director, The Textile Foundation, National Bureau of Standards, "Some Mechanical Properties of Fibers as Related to their Chemical Constitution."

● DYESTUFFS

Copies of *Dyestuffs*, quarterly publication of National Aniline & Chemical Co., Inc., 40 Rector St., New York, N. Y., for March, 1941, have recently been distributed. Articles are described by the following titles: Dermatitis from Wearing Apparel, Its Causes, Diagnosis and Prevention, by Louis Schwartz, medical director, U. S. Public Health Service; Embossing Acetate Rayon Materials; They Gave Us Paper, by Douglas C. McMurtrie; Dyeing with Madder from Ancient to Modern Times, by Karl Reinking; Leather, by Dr. Fred O'Flaherty (concluded); Dyeing Cotton, Linen and Wool Goods with Indigo (continued).

Wool Protein—

(Concluded from page 224)

The wide range of the measurements serves to emphasize the very large differences which may be found when different acids are used. If the position of each curve is characterized by the pH value at which half the maximum amount of acid (about 0.4 millimole per gram) is taken up, there is a difference of almost 2 pH units between the curves shown at the extremes of the series. Between these extremes the results obtained with the other acids are distributed with a fair degree of uniformity, with no evident tendency to resemble closely the results obtained with hydrochloric acid, the acid which has hitherto been most widely used in measuring the acid-combining properties of proteins.*

Attention must also be directed to another feature of many of the data represented in Figure 1. This is the combination of amounts of acid in excess of 0.82 millimole per g., the amount reported as the "maximum" obtained with hydrochloric acid. The maximum of 0.82 millimole per g. was sometimes exceeded by small amounts when high concentrations of acid (>0.2 *M.*) were used. Measurements of acid combined are susceptible to a relatively large experimental error when such high concentrations of acid are used, because (a) only a small proportion of the acid initially present is combined, (b) some acid hydrolysis of the protein cannot be avoided, and (c) exchanges of water between the partially hydrated fibers and the solutions, difficult to evaluate exactly, have a relatively large influence on the results obtained. For these reasons little weight was placed on these measurements, although they were consistent with the results of similar determinations on bone and hide collagen[2], and might be explained by the presence in proteins of extremely feeble basic groups, such as the amide groups of glutamine and asparagine, and the large content of peptide nitrogen. Special interest, therefore, attaches to the finding that in every case in which sufficiently high concentrations of other acids are used, a second step in the curve of acid combination apparently begins at pH values more acid than those at which the curve that covers the usually investigated range of combination flattens. Since this fairly well-marked "maximum" of about 0.82 millimole per g. has been shown to correspond closely to the primary amino content of the fibers, the additional uptake in more concentrated solutions must be accounted for by the more weakly basic groups or by combination by means of entirely different mechanisms. Such an alternative mechanism is suggested by the titration curve of wool with Orange II at 50°, shown in Fig. 6, in which the excess combination is even larger. The molecules of many dyes are known to be aggregated in aqueous solutions to a greater or lesser extent[40]. Although no evidence suggesting that Orange II is highly aggregated has ever been put forward, the failure of its solutions to obey Beer's law suggests that some degree of aggregation may occur in all but extremely dilute solutions of this dye. Combination of the fiber, at least in part, with aggregated dye anions, might then account for the large amounts taken up, and for the anomalous relation to pH of the amounts combined at high concentrations.

The displacement of the pH range in which the excess combination with most of the acids is found removes much of the uncertainty attending the earlier observation of similar excess combination with hydrochloric acid. All three of the possible sources of experimental error mentioned above are reduced or eliminated when the excess combination occurs in the presence of low concentrations of acid. In addition the excess found in concentrated solutions (1.03 — 0.82 = 0.21 in the case of naphthalenesulfonic acid) is far outside the limits of experimental error or of the possible range of effects on concentration due to exchange of water between fibers and solution.

Although the scatter of the points representing the combination of more than 0.8 millimole per g. is considerable, the portions of the curves which represent the second step of acid combination appear to run parallel to one another to about the same extent as do the main curves at higher pH values. The displacements of these parts of the curves thus appear to correspond, qualitatively at least, to the similar displacements of the parts of the curves which represent the combination of the first 0.82 millimole per g. Should further work establish that the concepts applied in this paper to the lower section of the curves may also be employed in the analysis of the excess combination of acid, the possibility is opened of studying in an aqueous environment the combination of these weakly basic groups with acid, and thus determining the number of these groups and the extent of their dissociation.

(To be continued)

*Comparable differences between the titration curves of wool with hydrochloric and with picric acids were found by Elöd[41].

• CLASSIFIED •

POSITION WANTED: Textile Chemist. Ph.D. with 18 years' experience dyeing, printing, permanent finishing, especially well versed in synthetic resin field, good research man, American citizen, age 44, married. Christian, speaks fluently French and German. New England or Metropolitan area preferred but will go anywhere. Write Box No. 303, American Dyestuff Reporter.

POSITION WANTED: Executive for Screen Plant. 18 years' experience, thorough knowledge of all phases of screen printing, including all methods of screen making, full knowledge of dyestuff formulation. Would like position with established firm or will organize screen plant. Write Box No. 304, American Dyestuff Reporter.

LABORATORY DRY CAN: For sale, mounted on strong wooden stand. Suitable for dyehouse or color shop. Write Box No. 309, American Dyestuff Reporter.